Determination of Organic Compounds Present in Airborne Particulate Matter

Final report prepared for
South Coast Air Quality Management District
in
completion of research under
SCAQMD contract no. 90024

by

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EQL Report 32

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Abstract

Fine organic aerosol samples ($d_p \leq 2.1\mu m$) were collected systematically during the entire year 1982 at four urban sites in the greater Los Angeles area and at one remote station: West Los Angeles, Downtown Los Angeles, Pasadena, Rubidoux, and San Nicolas Island. Samples were taken at 6-day intervals and composited to form monthly sample sets. The aerosol sample composites were subjected to high resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS). The objective is to quantify the abundance and seasonal variation of individual organic compounds that may be diagnostic for the contribution of particular emission sources to the ambient organic complex.

More than 80 organic compounds are quantified, including the series of n-alkanes, n-alkanoic acids, n-alkenoic acids, n-alkanals, and aliphatic dicarboxylic acids, as well as aromatic polycarboxylic acids, diterpenoids, polycyclic aromatic hydrocarbons, polycyclic aromatic ketones and quinones, nitrogen-containing organic compounds, and other organics.

Primary organic aerosol constituents are readily identified, revealing an annual pattern with high winter concentrations and low summer concentrations in the Los Angeles area. In contrast, dicarboxylic acids of likely secondary origin show a reverse pattern, with high concentrations in late spring/early summer. The total ambient annual average dicarboxylic acids concentration shows a steady increase when moving in the prevailing summer downwind direction from the most western urban sampling site (West Los Angeles) to the farthest eastern sampling location (Rubidoux), with an increase from 199 ng m^{-3} at West Los Angeles to 312 ng m^{-3} at Rubidoux. The occurrence of aromatic polycarboxylic acids in the fine particulate matter is discussed in detail in this study, including possible sources and formation pathways. The total aromatic polycarboxylic acid concentration reveals elevated summer concentrations when compared to the annual concentration cycle, indicating increased formation or/and emissions in summertime. Polycyclic aromatic hydrocarbons (PAH's), without exception, show low summer and high

winter concentrations; whereas, polycyclic aromatic ketones (PAK's) and quinones (PAQ's) show slightly increased input/formation during early summer, indicating possible atmospheric chemical reactions involving PAH's as precursor compounds. Molecular markers characteristic of wood smoke are identified, and their concentrations change by season in close agreement with prior estimates of the seasonal use of wood as a fuel.

The total mass concentration of identified aerosol organic compounds ranges from about 650 ng m^{-3} (West LA) to about 760 ng m^{-3} (Downtown LA) on an annual basis. Subdividing the total identified masses into their single compound classes reveals that n-alkanoic acids and aliphatic dicarboxylic acids make up the main portions quantified, followed by aromatic polycarboxylic acids, n-alkanes, diterpenoid acids, and polycyclic aromatic hydrocarbons.

This compilation of fine organic aerosol data on a molecular level provides an extensive catalog of the organic compounds quantified, covering an entire year. Further research is underway to characterize the organic aerosol released by primary emission sources in the Los Angeles area. That study will not only provide complete characterizations of these emissions sources on a molecular basis, but in addition will enable the identification and quantification of additional organic compounds in the same airborne particle samples which otherwise would have gone unidentified in the complexity of the organic matrix inherent in fine airbone particle samples. In the future, these data from the monitoring network can be used to evaluate the predictions of mathematical models for the atmospheric transport and reaction of organic aerosol constituents defined at a molecular level.

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Chapter 1

Determination of Organic Compounds Present in Airborne Particulate Matter

1.1 Introduction

Carbonaceous compounds constitute the largest contributor to the fine particulate matter in the atmosphere of highly industrialized and urbanized areas. Organic aerosol comprises 25% to 35% of total fine aerosol mass in the greater Los Angeles area (Gray et al., 1986). Fine particulate matter ($d_p \leq 2.1\mu m$) is known to be easily inhalable and has been considered responsible, together with gaseous pollutants, for the possible health effects connected with air pollutants (IARC, 1980; Miller, 1978; Yu and Yu, 1986). Elevated concentrations of organic compounds in fine respirable particles measured in many urbanized areas are of considerable concern because many of the organics present in the atmosphere are known mutagens (Chan et al., 1989; Pitts, 1983; Schuetzle, 1983) and carcinogens (IARC, 1980; Natusch, 1978; Ciccioli et al., 1989). Fine carbonaceous aerosols also play an important role in visibility deterioration, not only in urban areas like Los Angeles, but also in rural sites like the Grand Canyon (Hidy et al. 1974; Malm and Molenar, 1984; Mazurek et al., 1991; White and Macias, 1989; White and Roberts, 1977; Larson and Cass, 1989; Larson et al., 1989). The complete effects of fine particulate organic matter on the global biosphere are not yet well understood, but it is known that airborne fine carbon particles can travel over thousands of kilometers under suitable conditions before being removed from the atmosphere. Radiation budget studies in the Arctic show a decrease in reflection due to sunlight absorption by fine carbon particles deposited onto the snow and ice, and the origin of those particles can be traced to industrialized areas in North America and Europe (Clarke, 1989; Rahn et al., 1982).

In order to design an effective strategy for controlling fine primary organic particulate matter concentrations, knowledge of source/receptor relationships is

necessary. When compared to the composition of emission sources, a detailed chemical characterization of the atmospheric fine particles can be used to confirm anthropogenic and biogenic source contributions. The most straightforward means of confirming such source/receptor relationships is through the identification of organic compounds that may act as unique tracers for the presence of emissions from a particular source type within the ambient organic aerosol complex.

Existing ambient particle composition data are available for some groups of organic compounds (e.g., polycyclic aromatic hydrocarbons (PAHs), nitro–PAHs, normal alkanes, dicarboxylic acids, pesticides, etc.), but these data were acquired through the use of many different sampling devices under different sampling conditions (high–volume samplers, low–volume samplers, cascade impactors, cyclone separators, dichotomous samplers, different filter types, etc.), collected in different years and seasons. The laboratory procedures used to extract the organic material and to analyze the samples differ from investigator to investigator. As a result, there exists no consistent data set for airborne organic particles which includes a relatively complete characterization of the organic aerosol over a full annual cycle and at a representative number of sampling sites, spread over the area of investigation. A corresponding data set that describes the composition of the organic aerosol emitted from the important anthropogenic and biogenic sources likewise has not been available for comparison to ambient samples. Only a limited number of source test data are available which were actually taken under near–atmospheric conditions. Most of the source tests performed in the past overestimate the particle phase organics by cold trapping compounds which under atmospheric conditions would remain in the vapor phase, or alternatively underestimate particle phase organics due to sample collection at high temperatures. Hence, additional data are needed that have been collected in a way that is particularly suited to study the interrelation between source and receptor for individual organic compounds found in the atmospheric aerosol.

A data set suitable for comparison of source and ambient aerosol samples can be acquired through an ambient and source sampling program that is designed to describe the source/receptor relation adequately. Compatibility between the

source and ambient sampling procedures can be achieved if the same particle size separation devices, the same filter materials, and the same temperature conditions are employed during both the source and ambient sampling programs (Gray et al., 1986; Hildemann et al., 1991a, 1991b, Mazurek et al., 1989).

1.2 Objective

This report is part of a larger study designed to explore source/receptor relationships for organic aerosols on a molecular level. In the present work, the ambient fine organic aerosol in Southern California is characterized by high resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS). An entire annual cycle representing each month of the year 1982 is examined. In parallel research, source samples collected and analyzed by comparable methods also are being characterized. When combined these two research efforts will permit determination of the source origin of much of the primary organic aerosol based on molecular tracer techniques. The urban sampling sites studied are West Los Angeles, Downtown Los Angeles, Pasadena, and Rubidoux (near Riverside). San Nicolas Island is chosen to serve as a remote background station.

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Chapter 2

Ambient Sampling Program

2.1 Introduction

Organic particulate matter in the polluted urban atmosphere and in rural and remote areas is produced by combustion (pyrogenic), synthetic (anthropogenic products), geological (fossil fuels), natural (biogenic), and secondary (atmospheric chemical reaction) sources, which upon dispersion admix depending on the emission rates of the sources and their spatial proximity (e.g., Broddin et al., 1980; Ciccioli et al., 1989; Daisey et al., 1986; Grosjean, 1983, 1984; Jaenicke, 1980; Junge, 1977; Lamb et al., 1980; Matsumoto and Hanya, 1980; Mazurek and Simoneit, 1984; Mazurek et al., 1989, 1991; Pitts, 1983; Rahmdahl, 1983; Simoneit, 1977, 1979, 1980, 1984ab; Simoneit and Mazurek, 1989; Van Vaeck et al., 1979). The carbonaceous particulate matter is composed of numerous organic compounds: e.g., n-alkanes, n-alkanoic acids, dicarboxylic acids, ketones, alcohols, aldehydes, aromatics, polycyclic aromatic hydrocarbons, and many more. Organic matter together with macromolecular detritus (e.g., soot, charcoal, plant fragments, pollen, spores, microbes, etc.), trace metals, and ionic species comprise the complex aerosol constituents.

In order to obtain a representative picture of the chemical composition of the atmospheric fine particulate pollutant burden in the Los Angeles area, a program was designed to determine the organic aerosol composition at a molecular scale, and to cover the geographic area of interest in time and space.

2.2 Field Sampling Program

In 1982, field experiments were conducted that provide an extensive data set concerning ambient particulate pollutant concentrations (Gray et al., 1986). Ten stationary urban sampling sites were chosen extending from the western shoreline of the Pacific Ocean to the eastern end of the greater Los Angeles area (see Fig. 2.2.1). One offshore site, San Nicolas Island, was included to provide the background concentration data necessary to determine the pollutant concentrations present

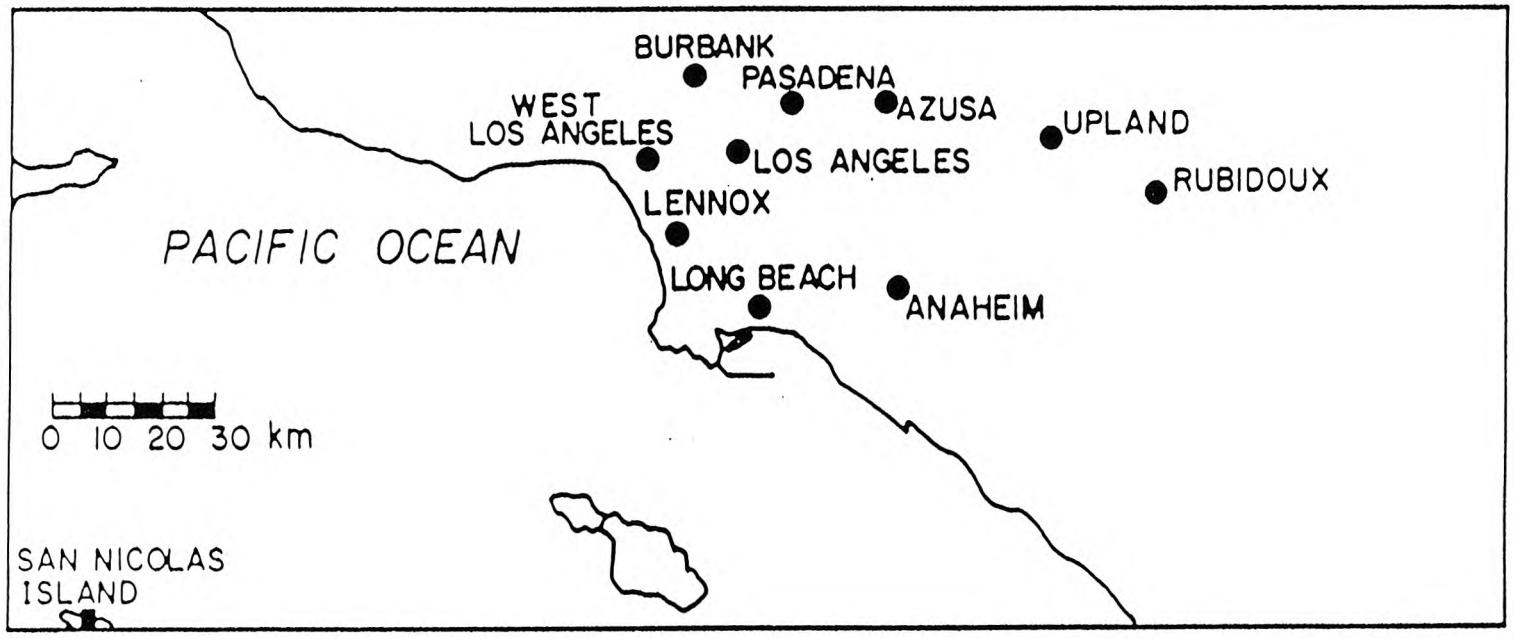

Fig. 2.2.1 Fine Particle Monitoring Network–1982.

in the atmosphere before air masses enter the Los Angeles area. Monthly averaged aerosol concentrations were constructed by combining samples collected for 24 hour periods at six day intervals for the entire calender year 1982 at each site. The sampling scheme was coordinated with the National Air Surveillance Network (NASN) high–volume sampling schedule. Thirty four trace elements, elemental carbon, organic carbon, and ionic species were measured. Additional filter samples were collected for subsequent identification of individual aerosol organic compounds.

The sampling equipment employed consisted of low volume (25.9 lpm) cyclone separators which removed particles with an aerodynamic diameter larger than 2.1 μm (John and Reischl, 1980). The sampled air was drawn through four parallel filter assemblies, at the flow rates shown in Fig. 2.2.2. The first filter assembly supplied with a back–up filter was used to collect fine particles for the bulk analysis of organic carbon (OC) and elemental carbon (EC). Quartz–fiber filters (Pallflex Tissuquartz 2500 QAO, 47-mm diameter) were used for carbon particle collection. The quartz filters were preheated prior to use at 600 °C for more than 2 h to reduce the carbon blank associated with new filters. The second filter assembly was used to collect fine particles for mass concentration and trace metals determination on Teflon filters (Membrana 0.5 μm pore size, 47-mm diameter). The Teflon filters were equilibrated at low relative humidity before and after sampling and then weighed repeatedly to obtain fine particle mass concentrations. The third parallel filter holder was used to collect fine particles on nuclepore filters, for determination of sulfates and nitrates by ion chromatography. Results from the bulk chemical analysis of these first three filter sets are reported by Gray et al. (1986). The last filter holder connected to the cyclone separator was operated at 10 lpm and loaded with pre–baked quartz–fiber filters (Pallflex Tissuquartz 2500 QAO, 47-mm diameter). This final filter set — from the West Los Angeles, Downtown Los Angeles, Pasadena, Rubidoux, and San Nicolas Island monitoring sites — was used during the present study for organic compound identification by means of HRGC and GC/MS, and will be discussed in greater detail in the following chapters.

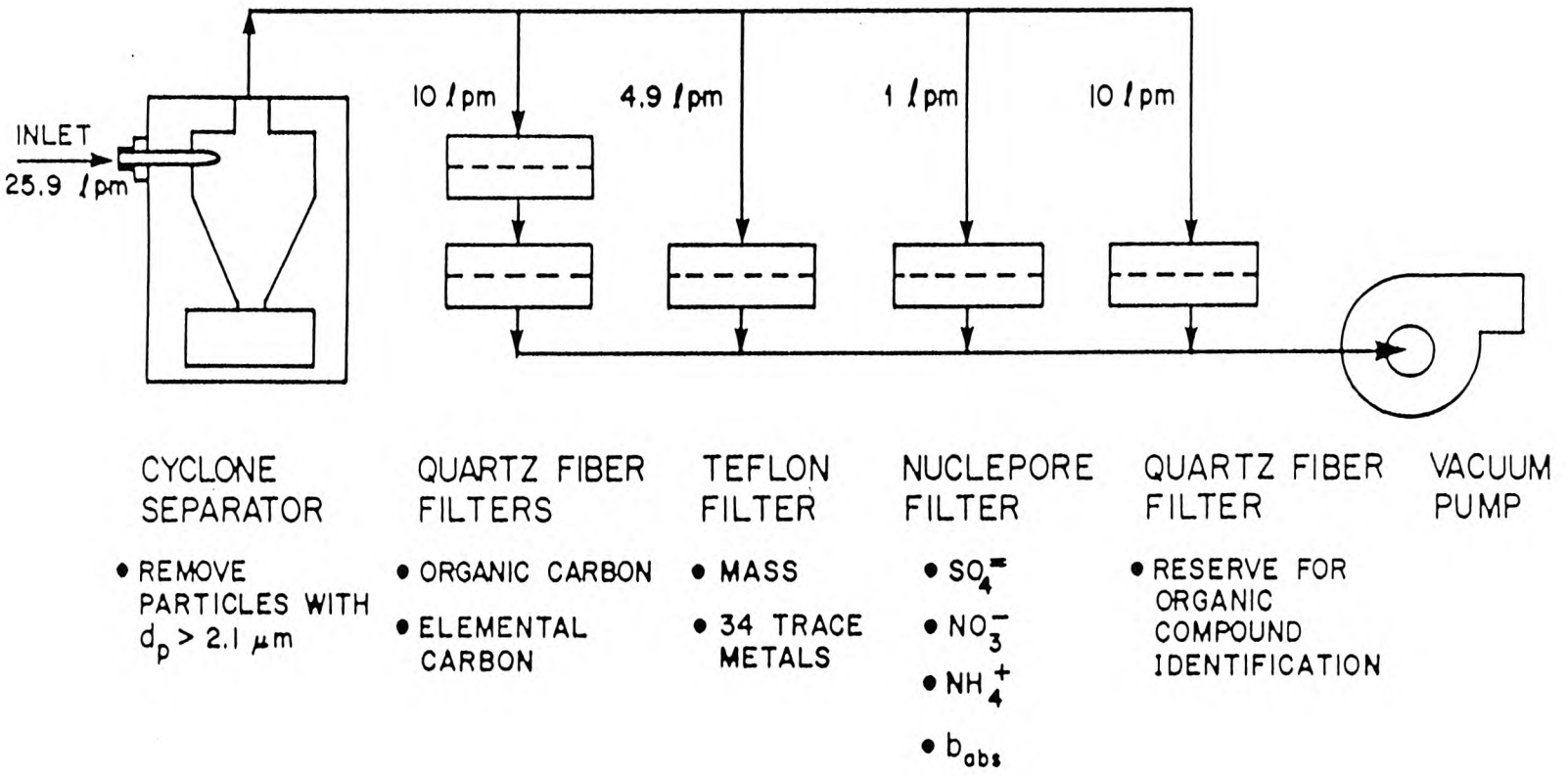

Fig. 2.2.2 Ambient Sampling Protocol–1982.

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Chapter 3

Bulk Chemical and Trace Element Concentrations

3.1 Introduction

Before investigating the compositional details of the fine organic aerosol, it is important to understand the major bulk constituents of the entire fine particle complex. By performing a material balance on the average monthly fine aerosol chemical composition at the different sampling sites, it is possible to put our later analysis of individual organic compound concentrations into a broader context.

3.2 Organic and Elemental Carbon

For all months and sampling sites organic and elemental carbon analysis was performed. The method used is described in detail by Huntzicker et al. (1982) and Johnson et al. (1981). This combustion/pyrolysis technique applied to the ambient samples discussed here is explained in more detail elsewhere (Gray et al., 1986). Data on atmospheric organic carbon (OC) and elemental carbon (EC) particle concentrations in Los Angeles were obtained for the year 1982. Annual average fine particle total carbon (TC = OC + EC) concentrations were measured and found to range from 2.02 μg m^{-3} at San Nicolas Island up to 12.16 μg m^{-3} at Downtown Los Angeles. Aerosol organic compounds typically contribute about 30% to the fine aerosol mass in the heavily populated western portion of the South Coast Air Basin, as seen in Fig. 3.2.1. These organic and elemental carbon data were later used as the basis of an extensive control strategy study for atmospheric fine primary carbon particle concentrations in the Los Angeles area (Gray, 1986).

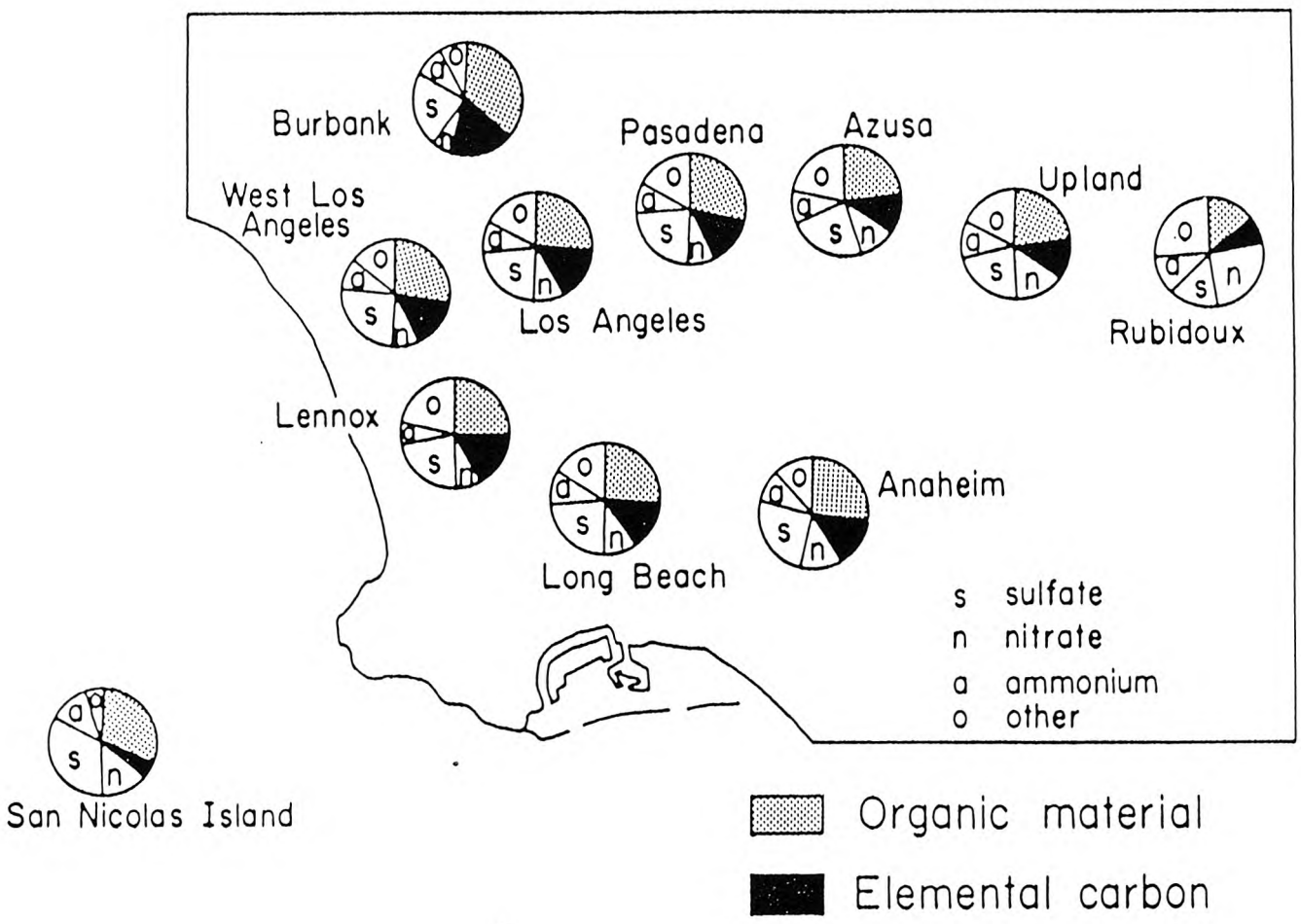

Fig. 3.2.1 **Material balance on the chemical composition of annual mean fine particle concentrations in the Los Angeles area–1982.**

3.3 Bulk Ionic Species

Bulk ionic aerosol constituents including ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}) were measured at all sites mentioned. Fig. 3.2.1 shows in a graphical fashion that these bulk ionic species sum to between 25% – 50% of the total annual fine particle mass concentration, depending on the sampling location. Sulfate and nitrate concentrations were determined by ion chromatography (Mueller et al., 1978) and the ammonium ion content was analyzed by the phenol–hypochlorite method (Solorzano, 1967).

3.4 Trace Elements

Thirty-four trace elements were routinely analyzed by X–ray fluorescence: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, and Pb. Certain of these trace metal data can be converted to their oxide form and used to estimate the mass concentration of soil-derived fine particles, which along with aerosol water make up the bulk of the *other* category shown in Fig. 3.2.1.

3.5 Mass Balance on the Chemical Composition of Urban Fine Aerosol

Material balances that describe the chemical composition of the aerosol at the different sampling sites were constructed as shown in Figures 3.5.1a-b. Of the bulk organic aerosol mass, typically 45 - 60% is extractable and elutable on the chromatographic column used according to the analytical procedures described earlier. HRGC and GC/MS-chromatograms produced from urban aerosol samples usually contain a large number of branched and cyclic hydrocarbons which are derived mainly from petroleum combustion that elute closely together producing an unresolved hump in the chromatograms, usually known as the unresolved complex mixture (UCM) (Simoneit, 1989). Hence, the elutable organics can be further subdivided into resolved (peaks) and unresolved (UCM) organic mass. The resolved portion of the elutable organics comprises about 23 - 29% of the elutable organic mass. From this resolved portion, about 75 - 85% can be identified as single molecular entities that are the subject of this study. Figures 3.5.1a-b show this mass

balance for the most western (West Los Angeles) and most eastern (Rubidoux) sampling sites. The most striking changes in comparing the mass balances for West Los Angeles and Rubidoux are the increase in total fine particle mass by nearly twofold, the explosive increase in particulate nitrate (an inorganic secondary formation product), and—on the molecular mass balance level—the pronounced increase in the aliphatic dicarboxylic acids at the Rubidoux sampling site which is downwind of the urbanized Los Angeles area.

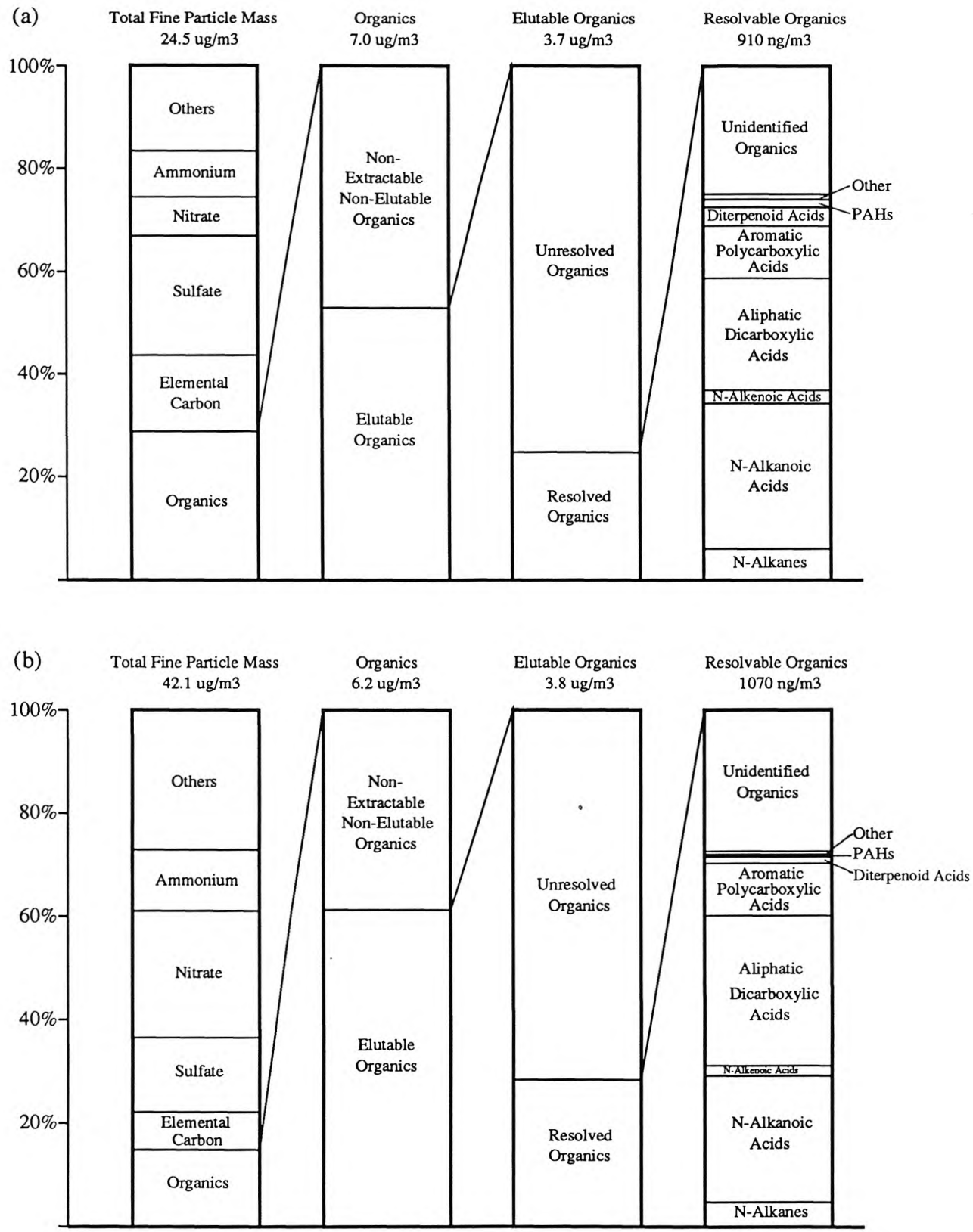

Fig. 3.5.1 Mass balance on the chemical composition of annual mean fine particle concentrations—1982 for a) West Los Angeles and b) Rubidoux (Riverside).

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Chapter 4

HRGC and GC/MS Analysis of the Elutable Organic Fraction

4.1 Introduction

Bulk carbon measurements mentioned earlier indicate that up to about 30% of the total fine particle mass in the Los Angeles atmosphere consists of organic material. In order to gain insight into the source origin and possible toxicity of this complex organic matrix, it is necessary to employ methods that subdivide the bulk organics into their single molecular organic entities. In the present section of this report, the organic aerosol extraction procedure and analysis techniques developed for use in this study will be described. Further details of the analytical methods are available elsewhere (Mazurek 1985; Mazurek et al., 1987, 1989).

4.2 Extraction Protocol for Ambient Samples

4.2.1 Solvent Selection

The bulk organic aerosol consists of a great number of organic compounds with different boiling points, polarities, reactivities, etc.. Depending on the overall goal of the sample analysis process, a large number of solvents or solvent mixtures are applicable. If the goal is to identify and quantify nonpolar compounds then a nonpolar solvent like hexane, cyclohexane, cyclopentane, or benzene commonly would be used. If the chemist is only interested in isolating polar compounds, then more polar solvents like chloroform, methylene chloride, isopropanol, ethanol, etc. could be used. The application of pure solvents to the extraction of fine particles collected on filters must face the problem that not only organic compounds are soluble, but also inorganic constituents like ammonium nitrate, for example. Extraction experiments conducted by Grosjean (1975) show that using binary extraction solvents (a mixture of a less polar with a more polar solvent) results in an extraction efficiency for polar compounds that is nearly as good as using only the polar solvent by itself, but with the benefit that the inorganic salts are less soluble. The major advantage is that the dielectric constant of the binary mixture is reduced compared

to the polar solvent, and hence, sulfates, nitrates, or ammonium salts will not be as soluble. Besides using the appropriate solvents/solvent mixtures, it is important to establish a very efficient extraction protocol. Since, for example, nonpolar organic compounds are less soluble in polar solvents and vice versa, successive extraction procedures can enhance the total extraction efficiency enormously. Using as a first extraction step a nonpolar solvent has the advantage that essentially all nonpolar compounds can be extracted. Following the second procedural extraction step with a polar solvent mixture (less polar/more polar solvents) — which is capable of extracting polar organic material nearly as efficiently as the polar solvent by itself but reduces the solubility of inorganic salts dramatically — the overall extraction process becomes quite efficient with total extraction efficiencies ranging from 90% to 100% for organic compounds, excluding high boiling compounds and compounds with molecular weights greater than 450 atomic mass units (Grosjean, 1975).

4.2.2 Extraction Protocol

Reagents. In the present study, distilled-in-glass high purity solvents were used for the entire extraction process and also for the preparation of standard mixtures. The procedural extraction solvents used were hexane, benzene, and isopropanol (Burdick and Jackson, Muskegon, Illinois). Authentic standard suites, necessary for organic compound identification and quantification, were prepared in our own laboratory. Benzene and toluene were the solvents used for the standard suite preparations. All standards were acquired with purities of 98% to 99% (Aldrich Chemical Co., Milwaukee, Wisconsin or from the collection of synthesized compounds of B.R.T. Simoneit).

Perdeuterated standard compounds used as recovery standards were acquired with purities of 98% to 99% (Merck, Sharpe and Dohme, Montreal, Quebec, Canada and Cambridge Isotope Laboratories, Cambridge, Massachusetts). The perdeuterated recovery standard added to the samples was n-tetracosane (n-$C_{24}D_{50}$). 1-Phenyldodecane was used as a coinjection standard. The relative response factors of all standard compounds were related to the coinjection standard. The derivatization of organic acids to produce their methyl ester analogues was conducted by the addition of diazomethane. Diazomethane was prepared from 1-methyl-3-

nitro-1-nitrosoguanidine. Due to its potential mutagenicity and flammability, the diazomethane preparation was done with great precaution.

Apparatus and Materials Used. All glassware used for sample extraction was annealed at 550 °C for at least 8 hours. Fittings and transfer lines were made of PTFE and solvent cleaned with distilled-in-glass grade methanol and dichloromethane. The transfer of solvent extracts from the extraction beaker to the collection flask was done with a specially designed vacuum transfer-line, described elsewhere (Mazurek et al., 1987). A rotary vacuum distillation unit was used for extract volume reduction, which was operated at a controlled vacuum of 640 mm Hg and temperature of 27 °C. The final volume reduction step was performed at ambient pressure with a gentle stream of precleaned nitrogen gas as promotor.

Extraction Procedure. Prior to extraction, the ambient aerosol filter samples were grouped according to calendar month with typically five 24-hour filter samples collected at a single monitoring site forming a single composite sample. Each filter sample set was spiked with predetermined amounts of the recovery standard (n-$C_{24}D_{50}$). The amount added was calculated using the OC data obtained by the combustion/pyrolysis technique for filter samples that were collected in parallel as described earlier. In this manner, the recovery standard was added to the filter composites in relation to the known organic aerosol masses collected. As a result, an amount of recovery standard could be added that was similar to that of individual compounds present in the samples. This step was necessary to ensure high quantification accuracy by FID- and MS-detection methods.

In order to conduct the extraction process for nonpolar and polar compounds at its optimum for each polarity level, a sequential extraction protocol was chosen. During the first chemical extraction step, hexane was added twice successively (2 × 15 ml). In the second phase of the extraction process, the loaded filters were three times successively exposed (3 × 15 ml) to benzene/isopropanol (2:1). At each of these single extraction steps the extraction process was supported by mild ultrasonic agitation for 10 min.. The ultrasonic agitation was performed with the temperature controlled at 20 °C. After each single extraction step, the

extract was transfered with the specially designed transfer-line (Mazurek et al., 1987) and combined. The total extract was then reduced to a volume of 3 to 5 ml by rotary vacuum distillation. The extract volume then was reduced further by gentle evaporation with a stream of high purity N_2 to a final volume of 300 to 500 μl. Following the volume determination, the extract was divided into two aliquots. One aliquot was reacted with freshly produced diazomethane to convert organic acids to their methyl ester analogues and other compounds having active hydrogens (e.g. phenols, enols) to their methoxy analogues. This will be termed the "acid + neutral" fraction. The underivatized aliquot will be referred to as the "neutral fraction". This terminology is adopted for chromatographic reasons. The fused-silica OV-1701 column which was used for the extract separation on the HRGC and GC/MS does not effectively permit the elution and separation of free organic acids (e.g. polar compounds). Therefore, relatively nonpolar (neutral) compounds are separated and elute from the column. The underivatized (neutral) extract aliquot, when injected onto this column, produces a chromatogram that contains rather "nonpolar" compounds—excluding the organic acids—while the derivatized "neutral + acid" extract aliquot gives as HRGC- and GC/MS-output a chromatogram containing both the "nonpolar and methylated acidic " compounds. After derivatization, the extracts were stored at -21 °C until HRGC- and GC/MS-analysis.

4.3 High-Resolution Gas Chromatography (HRGC)

4.3.1 System Configuration

The fine carbon particle extracts were analyzed using a Varian 4600 high-resolution gas chromatograph fitted with a Grob injector (splitless mode). The injector temperature was set to 300°C. A 30 meter fused silica OV-1701 column was used (bonded 86% dimethyl-[14%]-cyano- propyl phenyl polysiloxane, 25-μm film thickness, 0.32 mm i.d.; J & W Scientific, Rancho Cordova, CA). The HRGC was equipped with a flame ionization detector (FID) and operated at the maximum detector sensitivity of 10^{-12}mV.

4.3.2 System Operation

Gas Flow System. The gas flow through the chromatographic column was adjusted to 1.4 cm^3 min^{-1} (at 9.7 psi gauge pressure with a linear gas velocity of 29 cm sec^{-1}) using high purity helium as the carrier gas. Purified nitrogen gas was used as the detector make-up gas. The FID flame was produced with purified hydrogen and oxygen gas.

Temperature Programming. A sample extract aliquot (usually 1 μl) was injected onto the HRGC with an initial column temperature of 65 °C. The temperature setting was programmed in the following fashion: isothermal injection at 65 °C, isothermal hold at 65 °C for 10 min, programmed temperature increase at 10 °C/min to the final temperature of 275 °C, followed by isothermal hold for an additional 49 min.

4.4 Gas Chromatography/ Mass Spectrometry (GC/MS)

A Finnigan 4000 quadrupole gas chromatograph/ mass spectrometer interfaced with an INCOS data acquisition system was used. The organic compounds were ionized in the electron impact (EI) mode with an electron energy of 70 eV. The scanning frequency was set to 0.5 sec^{-1}, ranging from 50 to 550 daltons. The GC column used, temperature programming and time settings were identical to the HRGC-operating conditions.

4.5 Compound Identification

The compound identification and confirmation process was performed in a number of sequential processing steps. In step one, the compound identification was conducted by GC/MS-matches made to standard reference spectra libraries. The INCOS-data system that accompanies the GC/MS system is equipped with the National Institute of Standards and Technology (NIST) mass spectral reference library. An additional updated version of the NIST-library (version 2, 1990) with additional search options is maintained on an IBM-AT personal computer. In step two, the preliminary identification of compound peaks was confirmed by comparison to the mass fragmentation patterns and elution times of authentic standard

injections onto the HRGC and GC/MS systems used here. Compound identification can be characterized schematically in the following fashion: **(a) positive**, when the sample spectrum, standard spectrum and NIST-library spectrum were identical and also the retention time of the authentic standard and the sample compound were comparable; **(b) probable**, same as above, except no authentic standard was available, but the NIST-library spectrum agreed very well with the sample spectrum; **(c) possible**, same as above, except that the sample spectrum contained additional information, but the degree of overlap was of minor significance; **(d) tentative**, when the sample spectrum contained additional fragment peaks which could be due to noise or other overlapping compounds. The level of confidence in the identity of each compound is noted in Table 5.13.1, which also includes the annual average ambient concentrations for all compounds mentioned in this study.

4.6 Quantification

Identifiable compound peaks were quantified using the HRGC data system provided that the uncorrected compound mass was above 60 - 80 ng per sample based on comparison to the response of known amounts of 1-phenyldodecane as a coinjection standard and application of n-$C_{24}D_{50}$ as a recovery standard. Whenever the identified compound mass was below the above stated limit, or the seasonal variation of the compound under consideration showed some months below the above limit, quantification was instead conducted with the help of the "Selective Ion Monitoring" scheme (SIM) in connection with the MS system. Using the SIM scheme together with the MS chromatograms, the detection limit for the mass spectrometer is between 1.0 and 5.0 pg depending on the compound type and elution time. The uncorrected compound mass was then corrected according to the relative response of the compound to the detector used based on the injection of authentic standard suites. In this manner, two sets of response factors were generated, one for the FID-detector used in connection with the HRGC and another set for the mass spectrometer. Trace compounds like PAH's and many other compounds were principally quantified by GC/MS.

4.7 Sampling and Analysis Control

Many separate precautions are employed in order to ensure that high confidence can be placed in the data generated (Mazurek et al., 1987, 1989). A sampling and analysis control scheme was developed which included contamination control procedures applied to filter materials and sampling equipment, sampling device performance controls, field and laboratory blanks (method blanks), analysis method performance evaluation (e.g., application of perdeuterated surrogate spiking compounds, and recovery determinations for many standard compounds). Data quality was controlled by accuracy performance calculations and repeated replicate sample injections. Table 4.7.1. presents the methodology developed for the sampling and analysis of trace level organic aerosols. The table summarizes the possible problems and errors which could emerge during the sampling, extraction, injection, and quantification process, along with the steps that have been taken to prevent such problems.

Table 4.7.1 Sampling and Analysis Control for Organic Matter Determination in Fine Particle Samples

	Possible Errors during the Collection, Analysis, and Quantification of Samples	Measures to Control or Exclude Errors
	Sampling	
1	Quartz-filter manufacturing residues	Bake filters at 550 ° C for 2 hours or longer
2	Contamination of preheated filters during storage	Use only Petri dishes with heat treated aluminum foil liners for quartz-filter storage
3	Filter handling contaminants	Utilize precaution, use solvent washed tools
4	Contamination from sampling device	Solvent cleaning of all parts; use field blanks to identify contaminations from the sampling system
5	Leaks in sampling device, control overloading of filters	Measure flow rate through each filtering device before and after sampling
6	Power failure	Use of elapsed time meter to record run time
7	Alteration of collected sample	Place samples at ice temp. immediately after removal from sampler
	Sample Extraction	
8	Contamination from laboratory	Use laboratory blank filters to monitor[a]
9	Extraction temperature variations	Perform all extraction processes at controlled temperature
10	Impurities due to solvent artifacts	Use high purity solvents and verify purity of solvents[b]
11	Losses during transfer of extract	Use sealed transfer lines; apply only slight vacuum conditions
12	Unknown extraction efficiency	Add recovery standards to filter sample before extraction; conduct recovery experiments with standard compounds
13	Inaccuracies in extract volume determination	Use microliter syringe with small graduation units
14	Extract degradation during storage	Use heat treated glass vails and store sample extract at -21 ° C
	Sample Injection onto HRGC and GC/MS	
15	Inaccuracies in volume transfer to injector device	Use microliter syringe with 0.1 μl graduation units
16	Losses during injection	Use coinjection standard
	Compound Quantification	
17	Variations in system response	Accuracy determination, replicate sample injection[c]
18	Compound losses during extraction	Apply recovery calculations for mass quantification
19	Different detector response for each compound	Inject standard compounds and determine relative response factors (RRF's)

[a] To monitor the extraction process, blank quartz-filters were extracted in each sample extraction sequence.

[b] Solvent samples were concentrated and injected onto HRGC to check for possible solvent artifacts.

[c] Accuracy determinations were performed for different standard compounds and concentrations. The rel. standard deviation was between 4 and 8% (HRGC), depending on the standard amount injected.

4.8 References

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Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. (1989). Interpretation of High-Resolution Gas Chromatography and High-Resolution Gas Chromatography/Mass Spectrometry Data Acquired from Atmospheric Organic Aerosol Samples. *Aerosol Sci. Technol.* 10: 408–419.

Mazurek, M.A.; Simoneit, B.R.T.; Cass, G.R.; Gray, H.A. (1987). Quantitative High-Resolution Gas Chromatography and High-Resolution Gas Chromatography/Mass Spectrometry Analysis of Carbonaceous Fine Aerosol Particles. *Intern. J. Environ. Anal. Chem.* 29: 119–139.

Chapter 5

Results and Discussion
Fine Particulate Organic Compounds
—Ambient Concentrations—
Los Angeles 1982

5.1 Introduction

An ambient fine particle sample constitutes a very complex mixture, often with very low concentrations of trace organic compounds resulting from direct anthropogenic and biogenic source emissions, possible heterogeneous particle/gas phase reactions, and homogeneous particle/particle or gas phase/gas phase reactions producing particle phase compounds (usually called secondary atmospheric reactions that form secondary reaction products). In the present chapter, the quantitative results of the organic compounds identified in the Los Angeles area aerosol will be displayed and theories as to their possible origin will be discussed. Source attributions at the present time are speculative. An intensive study of the major anthropogenic primary emission sources in the Los Angeles area currently in progress will soon allow a more accurate assessment of the sources that contribute the individual compounds identified here.

5.2 Dilution and Windspeed Normalized Ambient Concentration Profiles

When seeking to identify the source of ambient organic fine particle ($d_p \leq 2.1\mu m$) compounds, it is useful to know if the emission rates, atmospheric formation rates, or atmospheric destruction rates for single compounds are steady during the whole year or if there are any seasonal periods in which sources or sinks increase. The knowledge of changing monthly averaged source or sink rates could suggest possible unexpected sources or source emission patterns, either of anthropogenic and biogenic origin or due to gas and/or particle phase atmospheric chemistry.

There are several possible methods for detecting seasonal variations in emissions, sources or sinks. One approach leads—with the help of meteorological data—

towards atmospheric transport modeling from which an estimate of the emission rates and emission variability can be made by backward calculation from variations seen at the receptor site of interest. If, as in our case, only the qualitative source variability by season is of concern, then it would be sufficient to have an inert primary tracer which is emitted over the whole year at a constant emission rate; then the concentration of that tracer in the area of concern would vary only due to seasonal changes in atmospheric dilution. If the ambient organic aerosol concentrations by month are divided by that tracer concentration that varies according to the atmospheric dilution potential, then the remaining seasonal variability in the organics concentration data mainly reflects changes in other processes such as source emission rates or atmospheric transformation rates.

Elemental carbon seems to be the prime candidate for an atmospheric dilution tracer in Los Angeles. It is known that most of the elemental carbon in the Los Angeles atmosphere is emitted by diesel autos and trucks (and also by stationary and off-road diesel engine sources), which exhibit a fairly constant emission pattern on a monthly basis throughout the year (Gray, 1986). Fine elemental carbon particles are chemically inert and are removed very slowly from the atmosphere, at rates comparable to the deposition rates for fine carbonaceous particles as a whole ($d_p \leq 2.1\mu m$). For this reason, it is possible to use ambient fine elemental carbon particle concentrations to eliminate seasonal meteorological variabilities by dividing the time series of single compound monthly averaged concentrations by the monthly average elemental carbon concentration measured at the same site. This technique provides a quick qualitative tool for the investigation of seasonal changes in source and sink patterns. This approach will be exploited throughout this work and will reveal interesting insights into the origin and fate of some airborne organic compounds that are present in the aerosol phase.

5.3 Normal Alkanes

In the industrialized modern world, there are many sources responsible for the input of n-alkanes into the atmosphere. Anthropogenic sources typically include the combustion of fossil fuels, wood and organic detritus. Meat cooking operations also have been identified as a source of small amounts of n-alkanes (Rogge et al., 1991). Biogenic sources include pollen, the epicuticular waxes of vascular plants, microorganisms (e.g. bacteria, fungi and fungal spores), and insects (Nilsson, et al., 1957; Hallgren and Larsson, 1963; Douglas and Eglinton, 1966; Tulloch, 1976; Simoneit, 1977; Simoneit and Eglinton, 1977; Oró et al., 1966; Weete, 1976; Jackson and Blomquist, 1976; Han and Calvin, 1969).

Normal alkanes of higher order originate from biological synthesis with carbon numbers ranging from n-C_{12} to n-C_{40} (Matsumoto and Hanya, 1980; Simoneit, 1989). Biosynthesized n-alkanes exhibit an odd carbon number predominance (e.g. C_{29}, C_{31}, C_{33} n-alkanes are more abundant in plant waxes than the C_{28}, C_{30}, and C_{32} n-alkanes), and are considered to be the stable end products of the biogenic and geochemical processes involving n-alkanoic acids as precursor compounds (Han and Calvin, 1969). In plants, the most favored route for n-alkane formation is the elongation of n-C_{16} and n-C_{18} fatty acids followed by decarboxylation reactions producing the n-alkane distribution found in plant waxes, with the dominant homologs being the n-C_{29} and n-C_{31} n-alkanes (Kolattukudy, 1970).

Defining the concentration ratio of odd to even numbered homologs as the **C**arbon **P**reference **I**ndex (**CPI**$_{odd}$), organic matter of recent biogenic origin reveals CPI values of 6-9 and more (Bray and Evans, 1961; Simoneit, 1978, 1989; Simoneit and Mazurek, 1982). During maturation of sedimentary organic material, the predominance of odd carbon alkanes is drastically reduced, such that fossil petroleum deposits show a CPI_{odd} value near unity, accompanied by a shift of the most abundant n- alkanes to lower carbon numbers with the carbon numbers of the most abundant homologs (C_{Max}) being 22 to 25 (Bray and Evans, 1961; Kvenvolden and Weiser, 1967). It is hypothesized that in sediments, step-by-step decarboxylation of the n-fatty acids occurs, producing the n-alkane distribution found in ancient sediments and crude oils (Cooper and Bray, 1963; Kvenvolden and Weiser,

1967; Matsuda and Koyama, 1977). Crude oils, and hence the emissions from the combustion of fossil fuels, exhibit as a result CPI_{odd} values close to 1.0 (Bray and Evans, 1961; Garza and Muth, 1974; Hauser and Pattison, 1972; Jackson et al., 1975; Simoneit, 1984, 1986, 1989). Hauser and Pattison (1972) determined the n-alkane distribution in ambient samples, motor oil, diesel fuel, gasoline, auto exhaust, and diesel soot. Interestingly, the mass median carbon number for n-alkanes is shifted from $\leq$ n-C_{19} in both diesel and gasoline fuels to n-C_{24} for auto exhaust and diesel soot. The mass median n-alkane for motor oil was determined to be $\geq$ C_{26}. Hence, partial combustion of motor oil may have contributed to the upward shift in mass median carbon number in vehicle exhaust as compared to vehicle fuel.

Normal alkanes originating from plant waxes, pollens, fungi, and insects show enhancements for the n-C_{25}, n-C_{27}, n-C_{29}, n-C_{31}, and n-C_{33} n-alkanes, whereas bacterial or algal derived n-alkanes are principally composed of odd alkane homologs between C_{11} - C_{25} (Simoneit, 1989; Nilsson et al., 1957). Often, n-C_{29} and n-C_{31} contribute up to 90% of all paraffins found in plant waxes, whereas n-alkanes from algae peak at n-C_{17} (Kolattukudy, 1970). Thus the distribution of n-alkanes provides some insight into the likely sources that contribute to the organic aerosol.

The input of n-alkanes into the atmosphere via fine particles ($d_p \leq 2.1\mu m$) occurs due to a number of physico–chemical processes. Combustion of fossil fuels and recent organic material is a common man–made input mechanism. Forest fires and forestry controlled burning provide other combustion-type emission mechanisms. Further biogenic emission mechanisms include the volatilization of lower n-alkanes, followed by condensation and adsorption onto preexisting particles; wind induced mechanical abrasion of plant foliage and bacterial degradation of plant life. Wind erosion of soil containing microorganisms, plant detritus and other organic material is a common mechanism, especially at rural sites (Simoneit, 1977; Doskey and Andren, 1986). Only two major source types are known to directly emit alkanes into the airborne fine particle mode. The most common mechanism is combustion, which very effectively emits into the fine mode. Mechanically induced emissions contribute most to the coarse airborne particle mode, but the continuous impact of mechanical forces on biogenic materials has been cited as producing a mechanical

input of plant waxes into the fine particle mode. Electron microscopic studies of leaf surfaces show that epicuticular waxes form a bloom on the surface and consist of wax protrusions which seem to be characteristic of each plant species. The size of the wax protrusions range from submicron to micron dimensions with various morphologies formed by different plants (Hall and Donaldson, 1963; Kolattukudy, 1970). Hall and Donaldson (1963) conducted experiments to determine epicuticular wax production and loss from leaves. They found in fields that after strong winds (30 knots and more), up to 50% of the leaf waxes were lost from the leaf surfaces.

The transport of anthropogenic submicron particles containing n-alkanes to remote areas has been investigated and reported in a number of publications (Eichmann et al., 1979; Eichmann et al., 1980; Gagosian and Peltzer, 1986; Gagosian et al., 1982; Schneider et al., 1983; Sicre et al., 1990; Simoneit, 1977). From the analysis of stable isotopes and typical pyrogenic–derived compounds like PAH's it can be shown that particle phase n-alkanes are relatively nonreactive particle constituents (Schneider et al., 1983).

5.3.1 Ambient n-Alkane Concentrations—1982.

Normal alkanes ranging from n-tricosane (n-C_{23}) to n-tetratriacontane (n-C_{34}) were found in the fine particle phase at the four urban sites studied here and also at our remote station at San Nicolas Island. The total n-alkane background concentrations at San Nicolas Island vary only slightly from summer (Jul. - Sep.) to winter (Oct. - Dec.) (1.3 ng m^{-3} versus 1.7 ng m^{-3}). The total n-alkane concentrations at the urban sites vary from location to location and between seasons. The highest total n-alkane concentrations were measured at Downtown Los Angeles followed by West Los Angeles, and Pasadena, reaching peak monthly averages of 146 ng m^{-3}. The lowest monthly average concentrations (20 ng m^{-3} to 40 ng m^{-3}) were found during the summer months (May - August 1982). The highest single n-alkane concentrations were found for n-pentacosane (n-C_{25}) and n-heneitriacontane (n-C_{31}) (see Fig. 5.3.1a-b).

The seasonal variation in the n-alkanes at all urban sites is basically the same regardless of the n-alkane under consideration. Fig. 5.3.2 shows a typical seasonal concentration pattern for the urban sites. The highest concentrations at West Los Angeles, Downtown Los Angeles, and Pasadena are found in the wintertime (see also Fig. 5.3.2 for the definition of seasons). The same trend can be seen at the less urbanized downwind site at Rubidoux (Riverside), except that the concentration of n-heneitriacontane (n-C_{31}; which may be dominated by local plant wax inputs) is higher in spring and summer than in the winter. A strong odd carbon number predominance is seen in Fig. 5.3.2 for the typical plant wax derived higher n-alkanes (C_{29} - C_{33}), indicating a significant input of recent biogenic origin.

Normalization (cf. Chap. 5.2) of the seasonal n-alkane data by taking their ratio to elemental carbon concentrations as a means of adjusting for atmospheric dilution shows more clearly the increased n-C_{31} atmospheric inputs during spring (see Fig. 5.3.3). Normalization of the complete n-alkane data shows that the normalized concentration profile for all n-alkanes as a sum (n-C_{23} to n-C_{34}) reveals a more or less even total emission rate over the whole year with slight minima in summer and slight maxima in winter (see Fig. 5.3.5). Normalized concentration profiles for most of the even numbered n-alkanes exhibit higher emissions during

wintertime with minima in July and August, indicating increased emissions from fossil fuel combustion in wintertime. Figure 5.3.6 shows as an example the normalized concentration profiles for n-C_{24} and n-C_{25} which have been identified as the major n-alkanes that are mainly derived from the combustion of fossil fuels. For odd n-alkanes $\geq$ n-C_{27}, the mid-year inputs slightly exceeded the winter inputs into the atmosphere, again suggesting increased emissions from higher plant life during the spring and summer seasons. In Fig. 5.3.7 the normalized n-alkane distributions for n-C_{29} and n-C_{31} are shown, which are considered to be the major plant wax n-alkanes.

The CPI_{odd} values (n-C_{25} to n-C_{34}) for all urban sites and months of the year are plotted in Fig. 5.3.4. The CPI_{odd} values vary from about 2.0 to 4.0 with somewhat higher values during spring (at Rubidoux) and summer (at West Los Angeles) indicating possibly higher relative inputs of biogenic–derived n-alkanes into the atmosphere at those times of the year.

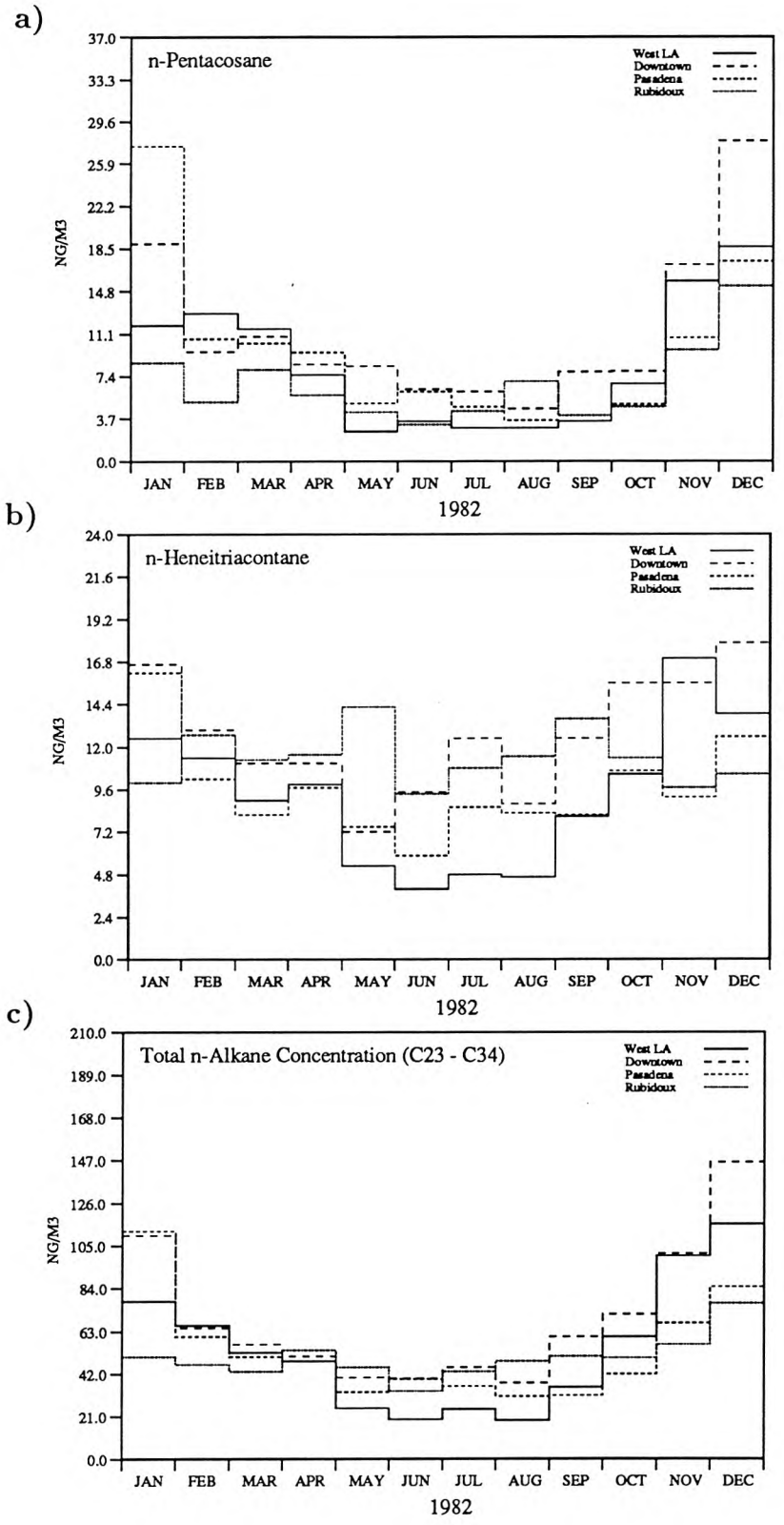

Fig. 5.3.1 Monthly averaged concentration profiles for a) n-pentacosane C_{25}, b) n-heneitriacontane C_{31}, and c) total n-alkanes C_{23} - C_{34}.

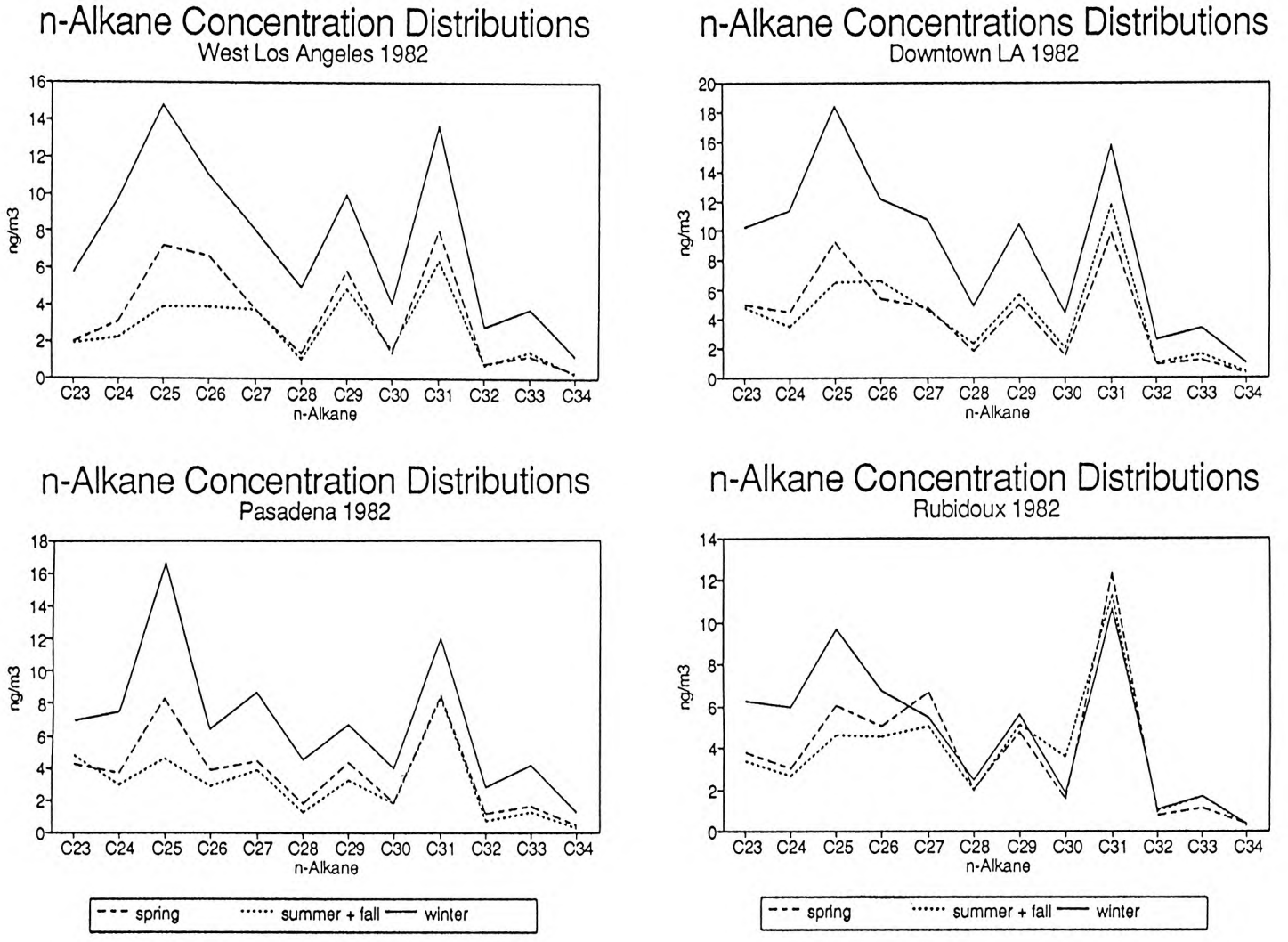

Fig. 5.3.2 Seasonal n-alkane concentration distributions (spring: March - May; summer + fall: June - October; winter: November - February)–1982.

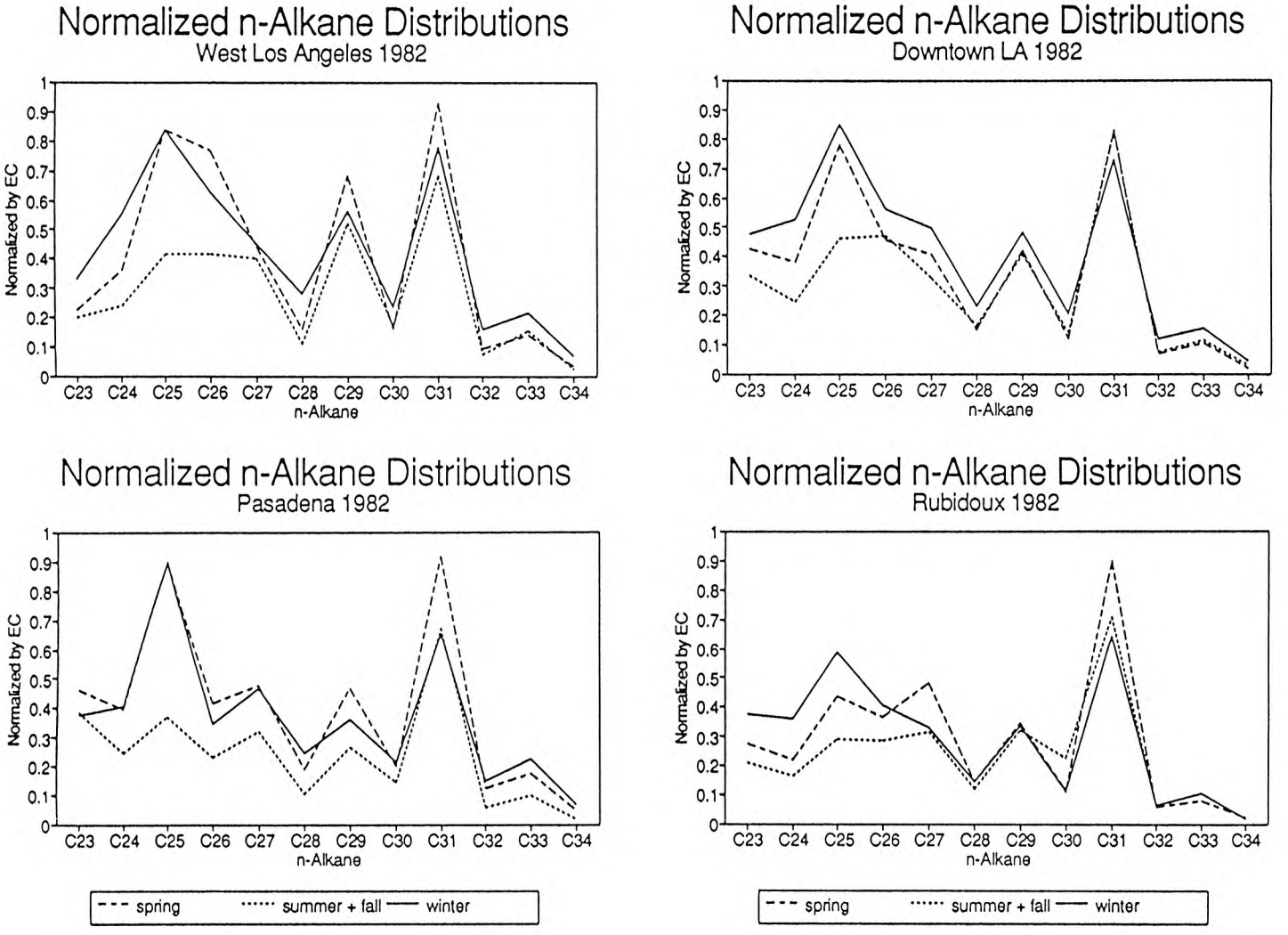

Fig. 5.3.3 Normalized seasonal n-alkane concentration distributions (spring: March - May; summer + fall: June - October; winter: November - February)–1982.

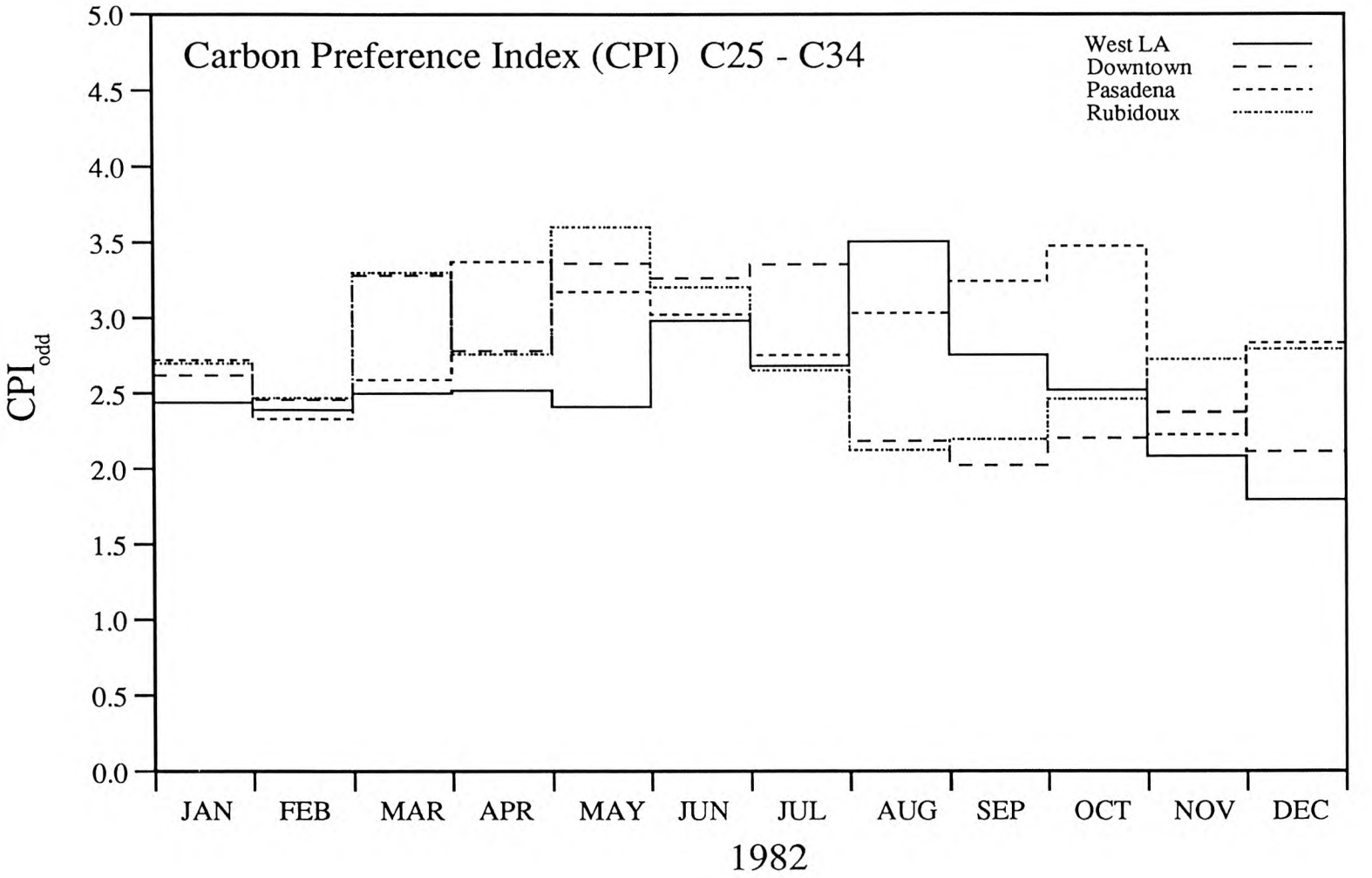

Fig. 5.3.4 Monthly CPI_{odd}-distribution patterns for ambient n-alkanes (n-C_{25} – n-C_{34})–1982.

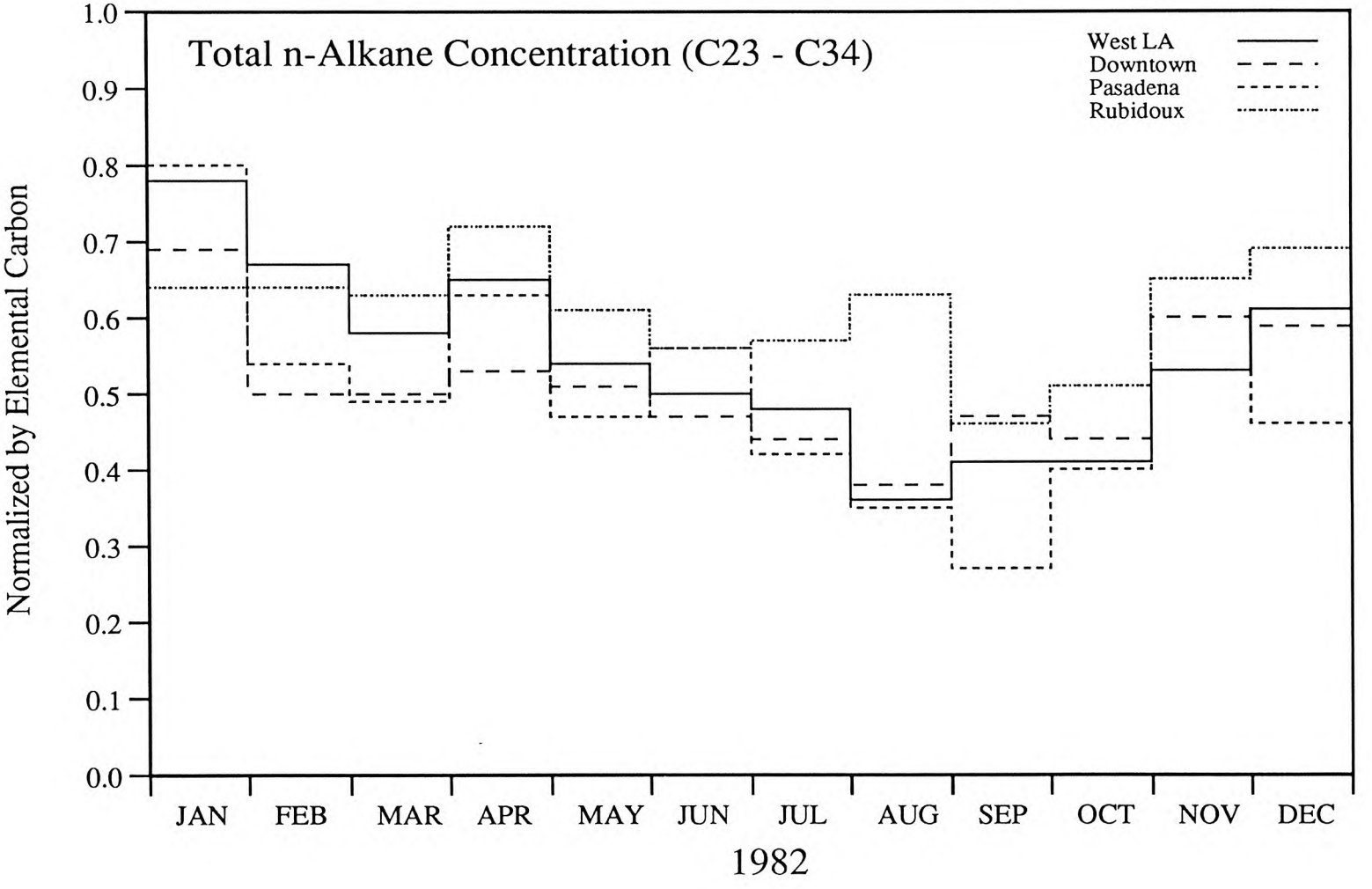

Fig. 5.3.5 Monthly normalized concentration profiles for total n-alkane (n-C_{23} – n-C_{34})–1982.

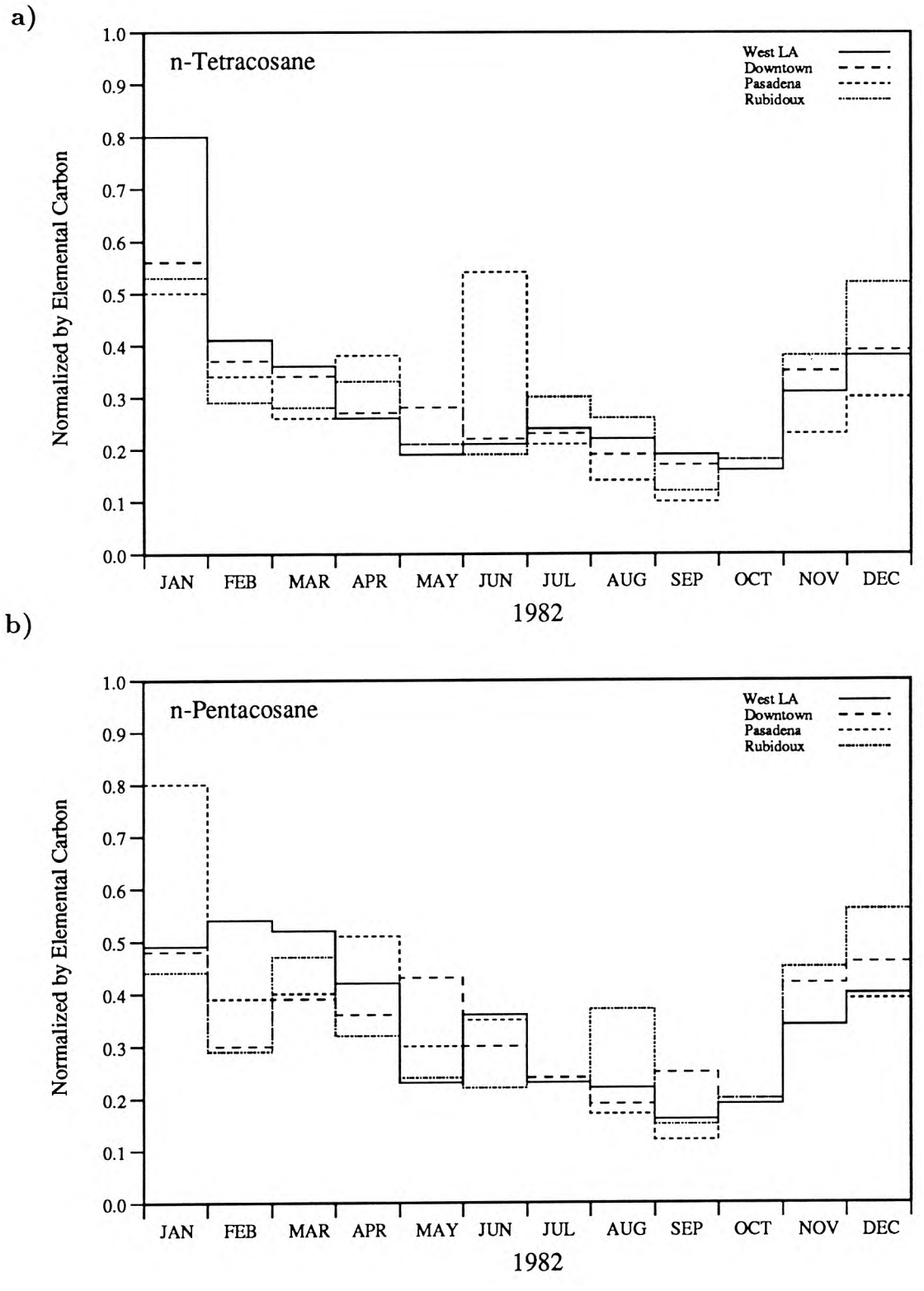

Fig. 5.3.6 Monthly normalized concentration profiles for a) n-tetracosane C_{24} and b) n-pentacosane C_{25}.

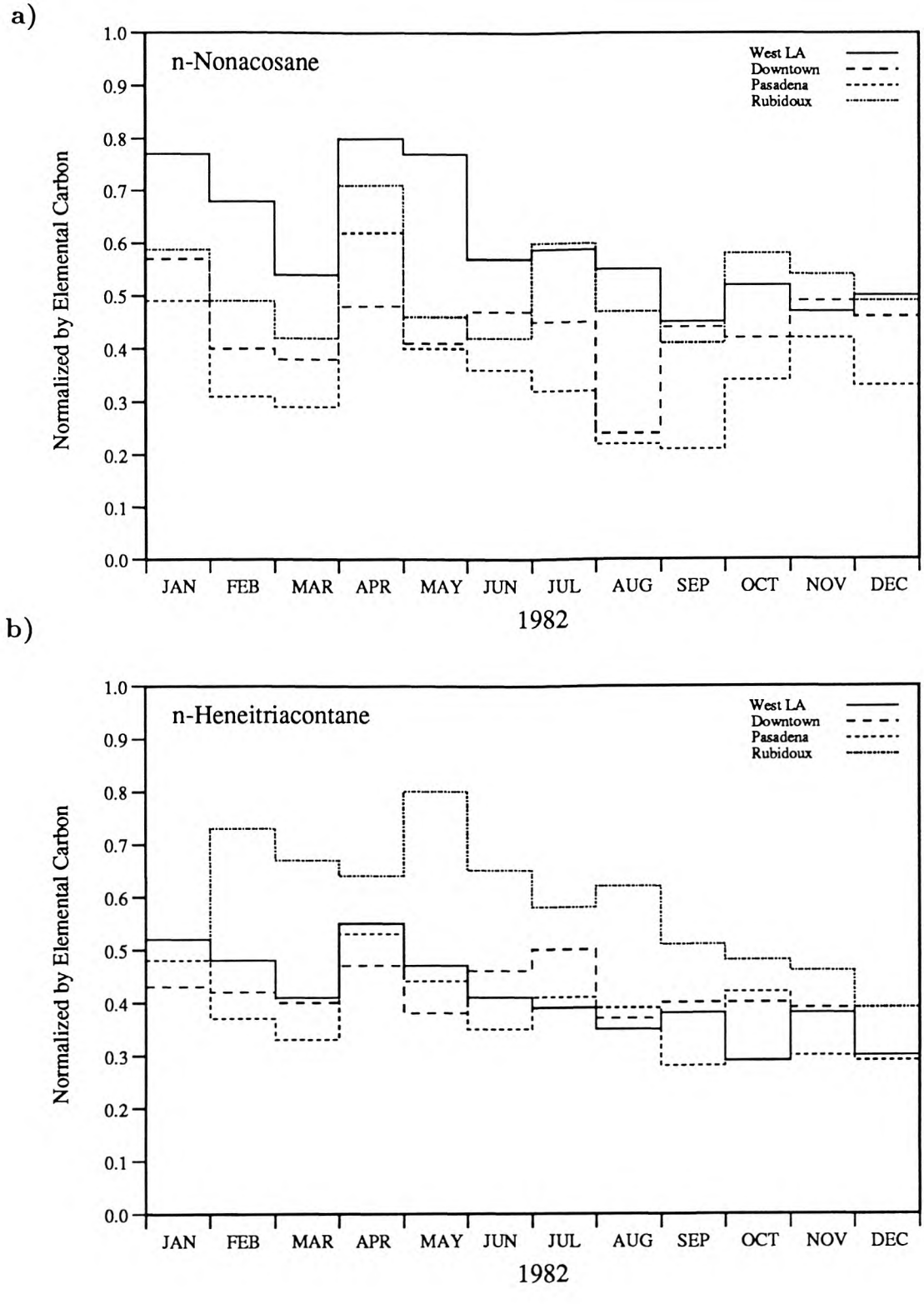

Fig. 5.3.7 Monthly normalized concentration profiles for a) n-nonacosane C_{29} and b) n-heneitriacontane C_{31}.

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5.4 Normal Alkanoic Acids

Atmospheric fine particle samples usually contain n-alkanoic acids ranging from n-C_9 to n-C_{30}. Sources contributing n-fatty acids to fine airborne particles are similar to the n-alkanes emission sources discussed in Chapter 5.3. Anthropogenic sources include the combustion of fossil fuels, wood and organic detritus. Recently, it was shown that meat cooking contributes significantly to the ambient n-alkanoic acid burden in the aerosol phase in Los Angeles (Rogge et al., 1991). The dominant n-alkanoic acids in meat smoke aerosol are n-C_{14}, n-C_{16}, and n-C_{18}, with highest emission rates for n-C_{16}, n-C_{18}. The release of n-alkanoic acids from fossil fuel combustion is a major contributor to the lower n-fatty acids with C_{Max} = n-C_{16} (Cooper and Bray, 1963; Simoneit, 1985, 1986).

Potential biogenic emission sources are numerous and practically identical to the sources for n-alkanes. Epicuticular plant waxes, fungi, bacteria, spores from fungi, bacterial spores, pollen, and algae are considered to be the main biogenic contributors (Brown et al., 1972; Ching and Ching, 1962; Jamieson and Reid, 1972; Kaneda, 1967; Kolattukudy, 1970; Laseter and Valle, 1971; Lechevalier, 1977; Matsumoto and Hanya, 1980; Morrison and Blick, 1967; Simoneit, 1977, 1989; Simoneit et al., 1988; Shaw, 1974). Interestingly, even though the synthesis of n-fatty acids and n-alkanes in plant leaves proceeds via elongation–decarboxylation processes of n-C_{16} and n-C_{18} fatty acids, plant wax acids consist usually of much longer homologs (n-C_{20} to n-C_{32}) (Hall and Donaldson, 1963; Kolattukudy, 1970; Simoneit, 1989). In contrast to the plant waxes, seeds (and seed oils, e.g. cooking oil), plant organelles, leaf cells, chloroplasts and pollen contain mainly n-C_{16}, n-$C_{16:1}$, n-C_{18}, and n-$C_{18:3}$ n-fatty acids (Ching and Ching, 1962; Hitchcock and Nichols, 1971; Jamieson and Reid, 1972). Bacterial and some algal detritus favour mostly n-alkanoic acids $\leq$ n-C_{20} (Hitchcock and Nichols, 1971; Kaneda, 1967; Simoneit, 1989). Fungal spores contain usually n-fatty acids between n-C_{14} and n-C_{22} (Laseter and Valle, 1977).

Biosynthetic n-fatty acids exhibit a strong even to odd carbon number predominance (CPI_{even} values of 30.0 and more are typical; see Simoneit, 1989). Due to the fact that plant wax acids are of much longer chain length than bacterial

and algal n-fatty acids, the contribution of higher plants to the aerosol burden can be viewed qualitatively by defining CPI_{even} in the range from n-C_{21} to n-C_{30} as an indicator. Wood combustion also contributes n-alkanoic acids with an even carbon number predominance in the higher molecular weight range from n-C_{21} to n-C_{30} (Standley and Simoneit, 1987). Fortunately, wood combustion in Los Angeles will be shown to be significant only in wintertime (Gray, 1986). Hence, CPI_{even} analysis of higher molecular weight n-alkanoic acids concentration data could eventually become useful as an indicator of biological input to the aerosol burden during the spring and summer seasons. The actual influence of bacterial, algal, and spore n-fatty acids cannot be determined by using CPI_{even} for n-C_{12} to n-C_{20}, since anthropogenic sources like wood combustion, vehicle emissions and meat cooking complicate data interpretation in this lower molecular weight range. So little is known at this time about the emissions of n-alkanoic acids from different source types , that carbon preference indices are of limited value in evaluating the magnitude of anthropogenic versus natural sources.

5.4.1 Ambient n-Alkanoic Acid Concentrations—1982.

Normal n-alkanoic acids ranging from n-hexanoic acid (n-C_6) to n-triacontanoic acid (n-C_{30}) have been identified in the remote (San Nicolas Island) and urbanized target areas (West Los Angeles, Downtown Los Angeles, Pasadena, and Rubidoux) of this study. Normal alkanoic acids smaller in chain length than n-nonanoic acid (n-C_9) have relatively high vapor pressures; therefore, no quantitative description can be provided for those compounds without knowing their partitioning coefficients between the gas and particle phase under ambient conditions.

At our background station at San Nicolas Island, total n-alkanoic acid concentrations ranging from 19.5 ng m^{-3} during summer to 25.6 ng m^{-3} during the winter season were measured. The highest concentrations were found for even carbon number n-alkanoic acids with the peak concentration observed for n-C_{16}, followed by n-C_{18}, and n-C_{14} n-fatty acids. In winter, the n-fatty acid concentrations for n-C_{14}, n-C_{24}, and n-C_{26} are higher than in the summer. The CPI_{even} value in the higher range from n-C_{21} to n-C_{30} increases slightly from 4.1 in summer to 5.1 in winter. Wood combustion on San Nicolas Island cannot be responsible for that shift since no wood smoke markers (diterpenoid acids, see Chapter 5.8) were found.

The urban total n-alkanoic acid concentrations during the summer season are as low as 150 ng m^{-3} (August, September), whereas during wintertime, concentrations are more than tripled (550 ng m^{-3}, see Fig. 5.4.1). The highest concentrations of single n-alkanoic acids for all sites and seasons are found for the n-C_{16} acid (100 - 250 ng m^{-3}), followed by the n-C_{18} acid (30 - 100 ng m^{-3}) (see Figures 5.4.2a-b). To emphasize the distinctly different concentration pattern for higher n-alkanoic acids, Figures 5.4.3a-b show the annual concentration distributions for n-tetracosanoic acid and n-hexacosanoic acid, revealing very low summer concentrations with greatly increased winter concentrations. This increased winter concentration may not be due entirely to enhanced emission activities in winter. Instead, some of the increase could be due to poorer atmospheric dispersion conditions in winter. Seasonal n-alkanoic acid concentration distributions (spring, summer/fall, and winter) are summarized in Fig. 5.4.4. n-Alkanoic acids concentrations

normalized by elemental carbon concentrations are shown in Figures 5.4.5a-c. The normalized concentration pattern shows increased emission inputs for all n-alkanoic acids as a group during spring and summer time (Fig. 5.4.5c). By investigating the normalized ambient distribution pattern over the whole year for each single n-alkanoic acid, it is seen that these compounds fall into two groups: n-alkanoic acids < n-C_{20} which show typical maxima in spring and summer, and in contrast, higher n-alkanoic acids (n-C_{20} to n-C_{28}) which show higher atmospheric inputs during the winter months. In Figures 5.4.5a-b, normalization by elemental carbon concentrations to remove dilution effects demonstrates very clearly the distinctly different input characteristics for lower (n-C_9 - n-C_{19}) and higher (n-C_{20} - n-C_{30}) n-fatty acids. Directing attention towards single members of these two distinct n-fatty acids groups basically reveals the same behavior (Figures 5.4.6a-b). While the dominant emitters of the n-alkanoic acids have yet to be determined precisely, it is probable that different sources will be found to dominate the lower (n-C_9 - n-C_{19}) versus higher (n-C_{20} - n-C_{30}) n-fatty acids emissions. Additional figures in this series appear in Appendices A2 and B2.

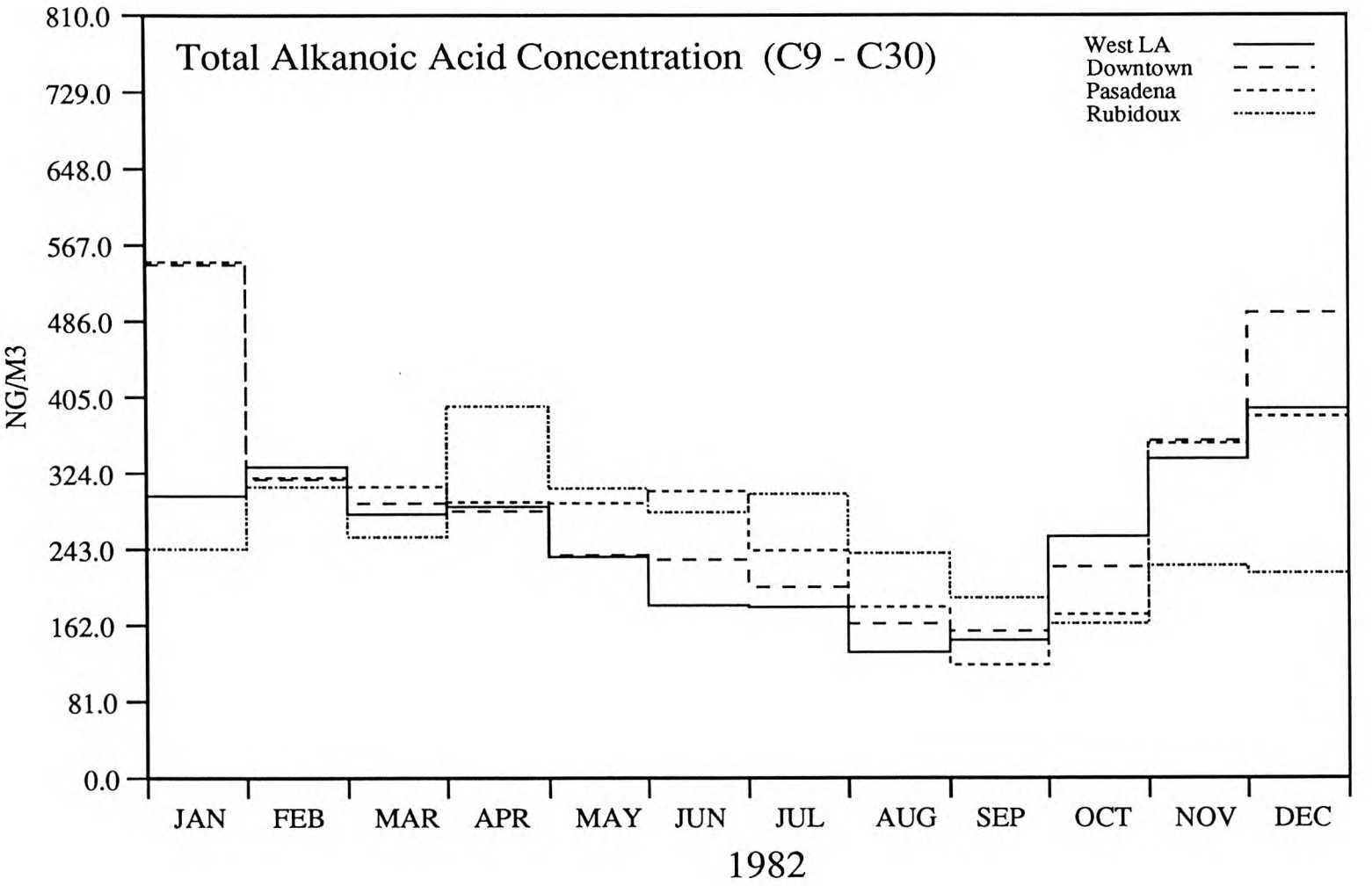
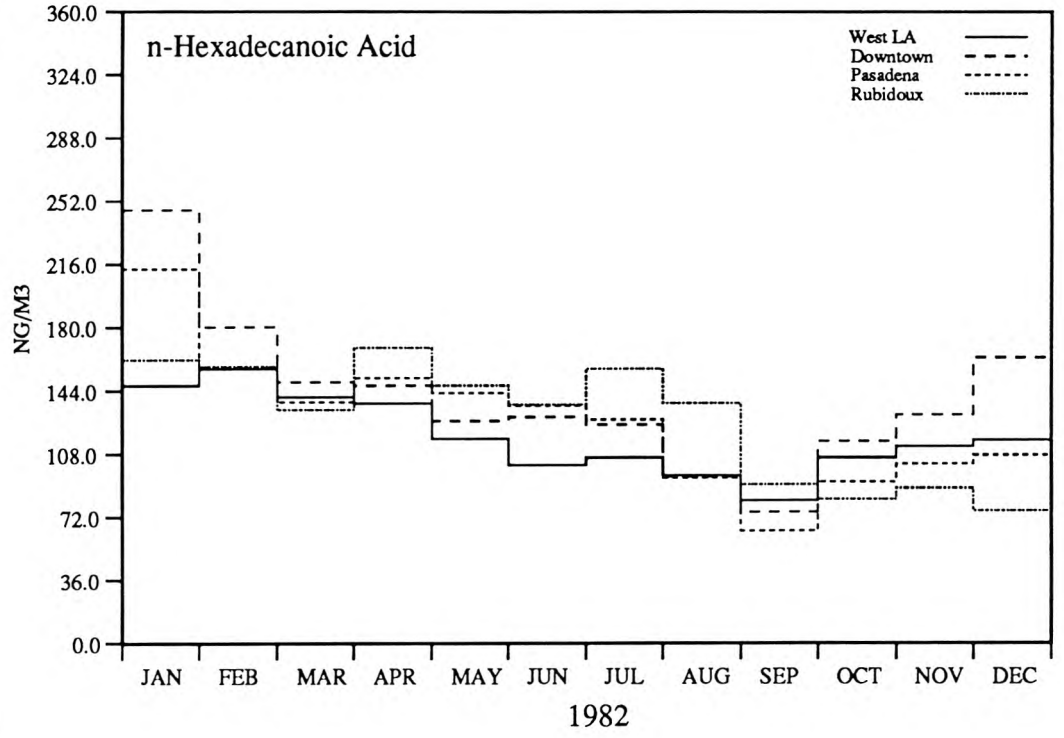


Fig. 5.4.1 Total monthly averaged n-alkanoic acid concentration distributions—1982.

a)



b)

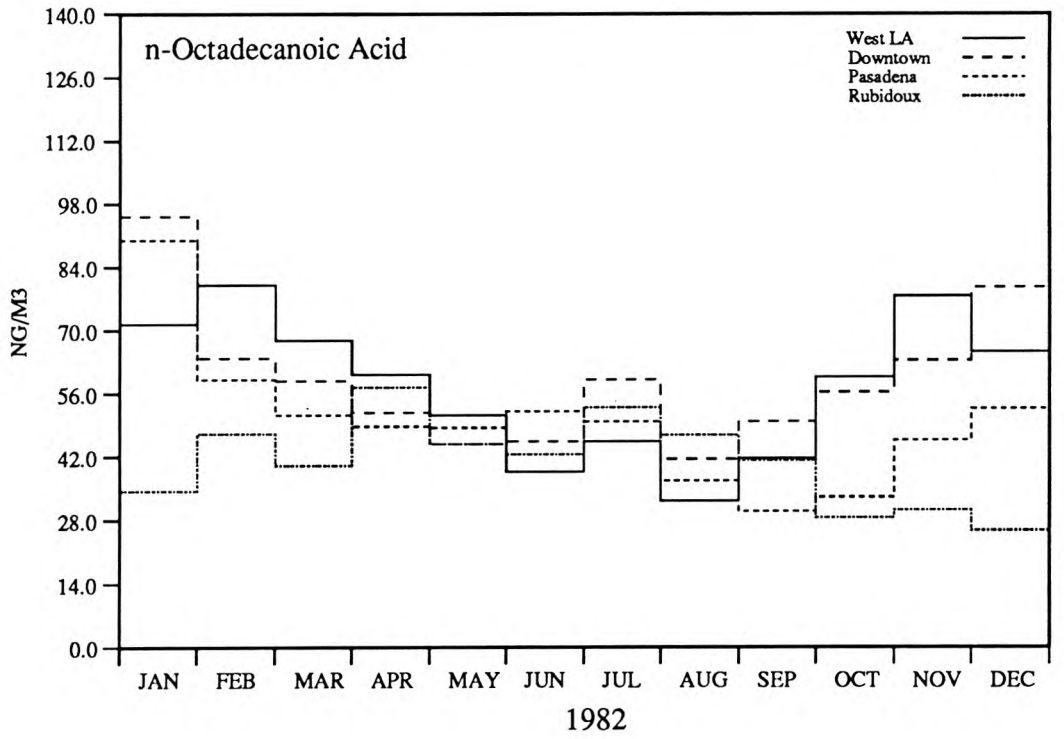


Fig. 5.4.2 Monthly averaged concentration profiles for a) n-hexadecanoic acid C_{16} and b) n-octadecanoic acid C_{18}.

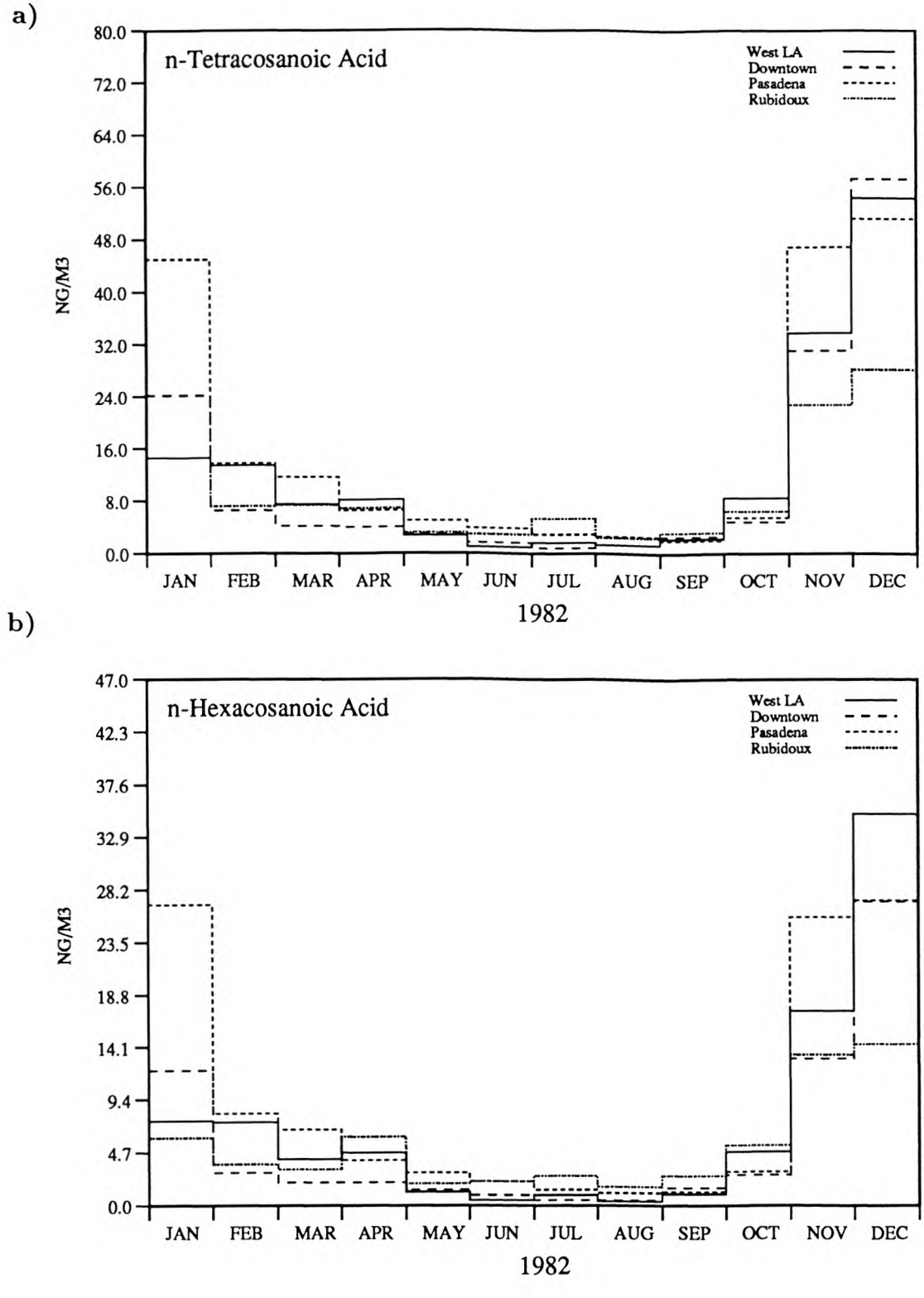


Fig. 5.4.3 Monthly averaged concentration profiles for a) n-tetracosanoic acid C_{24} and b) n-hexacosanoic acid C_{26}.

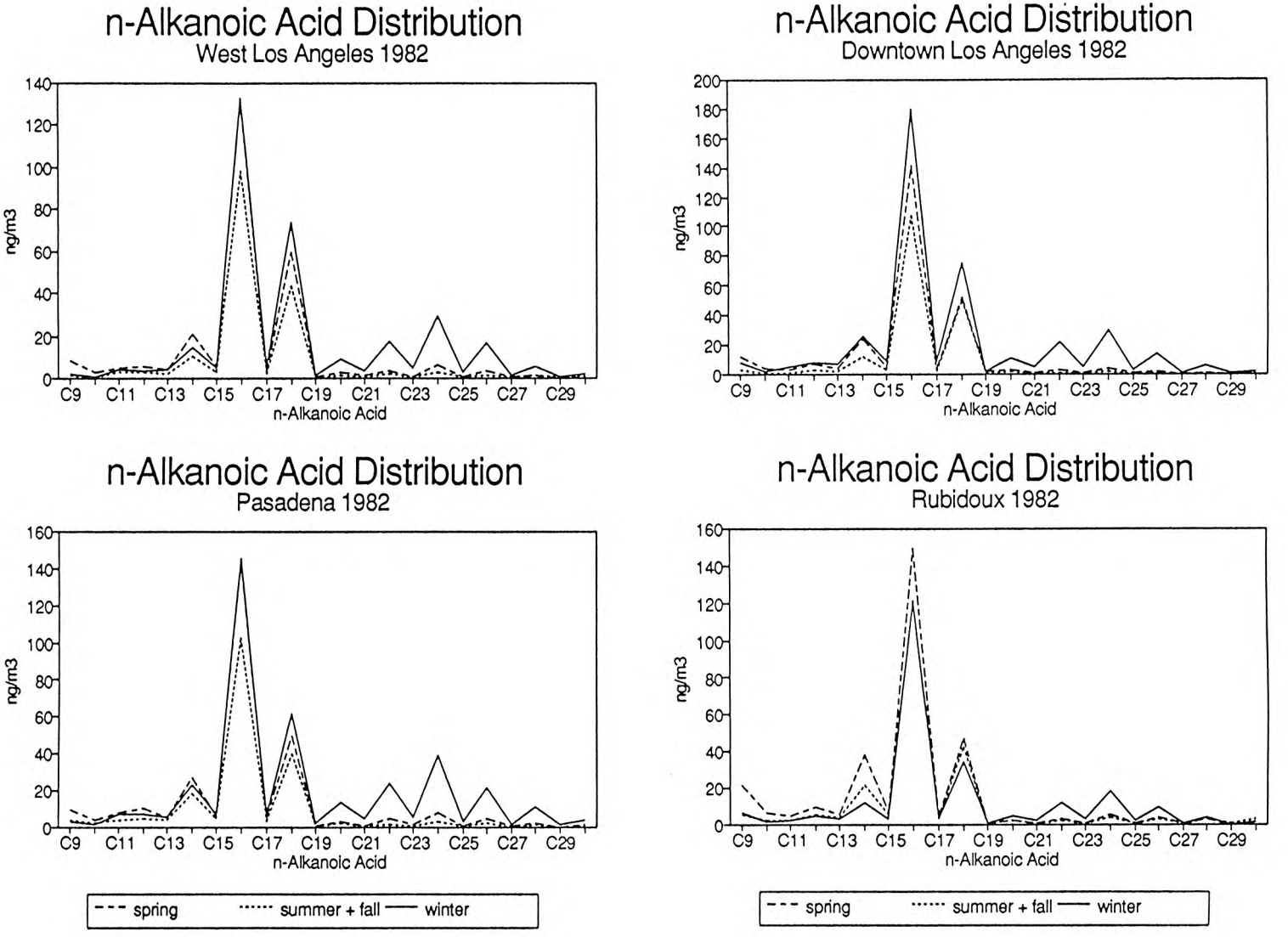


Fig. 5.4.4 Seasonal n-alkanoic acid concentration distributions (spring: March - May; summer + fall: June - October; winter: November - February)–1982.

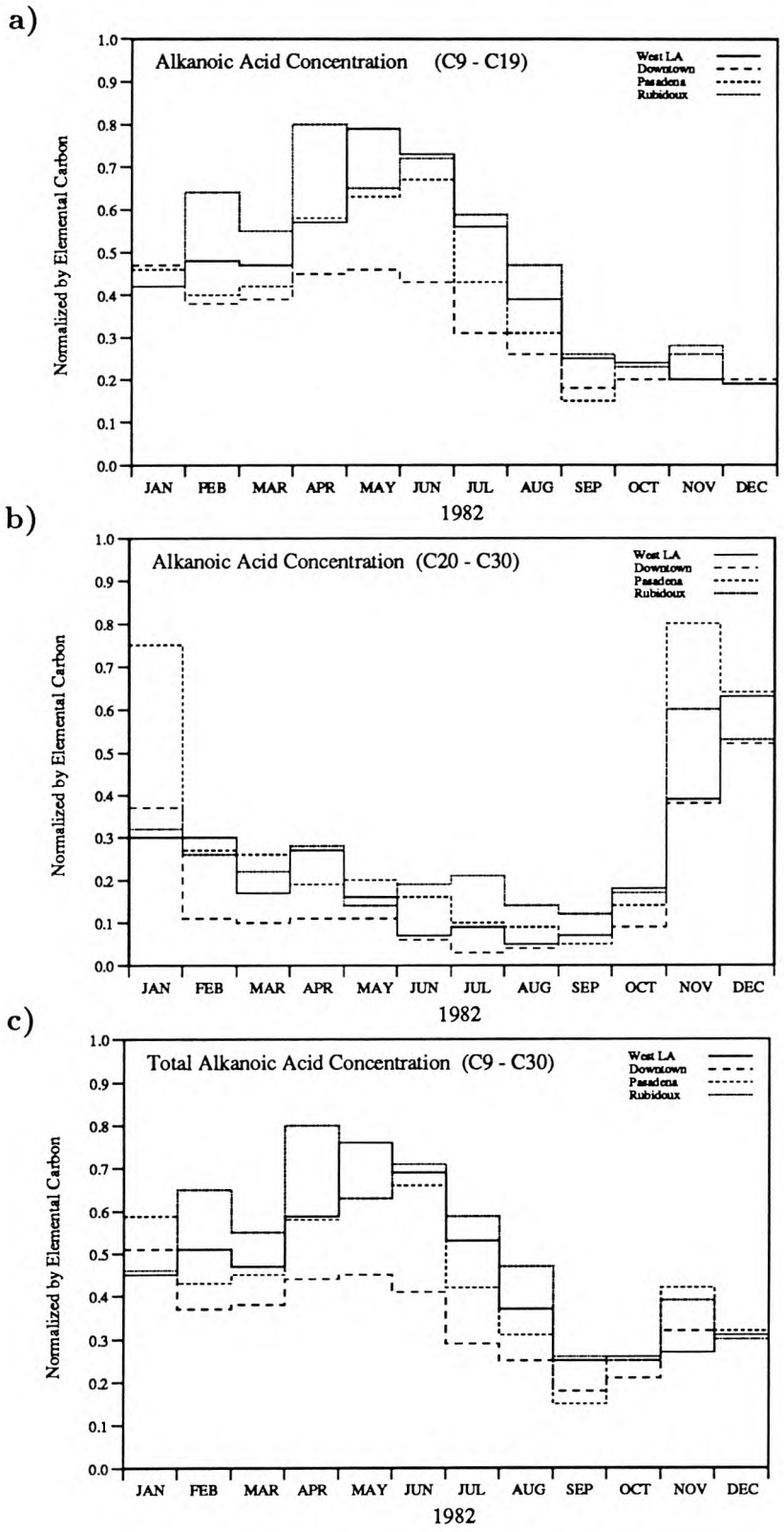


Fig. 5.4.5 Monthly normalized concentration profiles for a) n-alkanoic acids range C_9 - C_{19}, b) n-alkanoic acids range C_{20} - C_{30}, and c) total n-alkanoic acids range C_9 - C_{30}.

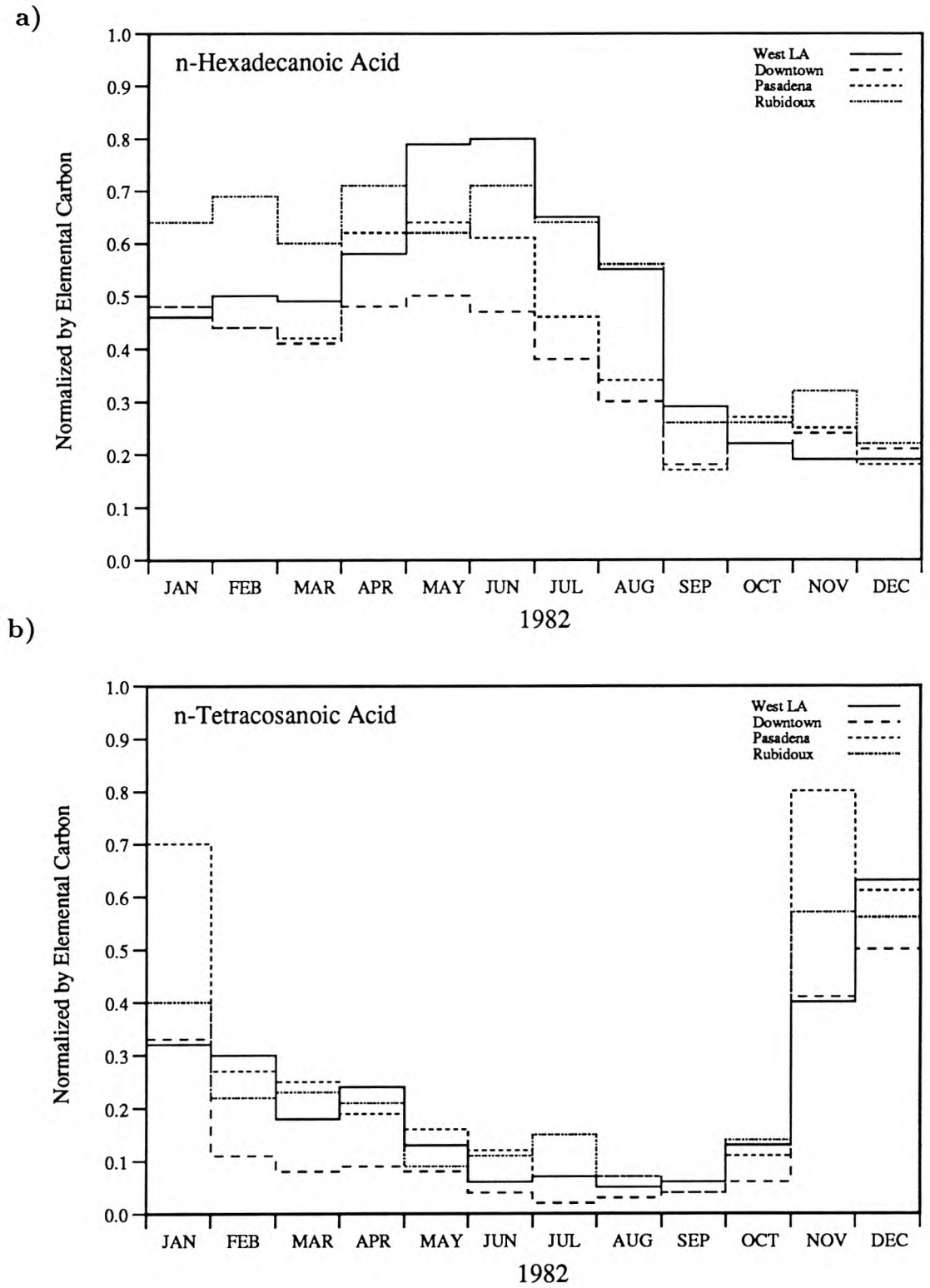


Fig. 5.4.6 Monthly normalized concentration profiles for a) n-hexadecanoic acid C_{16} and b) n-tetracosanoic acid C_{24}.

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5.5 Normal Alkenoic Acids

Monounsaturated ($C_{n:1}$), diunsaturated ($C_{n:2}$), and polyunsaturated fatty acids are known to occur in higher plant life, including seeds, pollen, leaves and other plant parts (Ching and Ching, 1962; Hitchcock and Nichols, 1971; Jamieson and Reid, 1972; Laseter and Valle, 1971). Phytoplankton and bacteria contain unsaturated n-fatty acids (Hitchcock and Nichols, 1971; Lechevalier, 1977; Shaw, 1974). In addition, animal fat contains large amounts of palmitoleic ($C_{16:1}$) and oleic ($C_{18:1}$) acids (Lovern, 1965).

Normal alkenoic acids are emitted to the atmosphere during processing and combustion of plant and animal constituents. Recently, it has been shown that meat cooking is an important source for unsaturated fatty acids emissions, especially for oleic and palmitoleic acid (Rogge et al., 1991), and it was speculated that cooking with seed oils and margarine or animal fat would likewise release such aerosols to the atmosphere. Cigarette smoke is another possible source for multiunsaturated C_{18} fatty acids (Johnstone and Plimmer, 1959; Walters et al., 1975).

Once emitted into the atmosphere, unsaturated fatty acids are likely to be attacked by oxidants (e.g. O_3) and radicals, producing aldehydes, carboxylic acids, and dicarboxylic acids. The most commonly emitted unsaturated fatty acid is Δ^9-$C_{18:1}$ (oleic acid), which is often the only identified n-alkenoic acid in atmosperic particle samples. Kawamura and Gagosian (1987), and Kawamura and Kaplan (1987) proposed that oleic acid undergoes photochemically induced oxidation yielding ω-oxocarboxylic acids, aldehydes, n-alkanoic acids, and dicarboxylic acids with predominantely C_9 species. Up to the present time, the only laboratory experiments regarding oleic acid oxidation have been performed in the liquid phase with ozone as the oxidizing agent (Killops, 1986). Aldehydes, carboxylic acids, and dicarboxylic acids were the main oxidation products with the expected cleavage of the Δ^9 double bond. Interestingly, an additional increase in ozone concentration enhanced the oxidation of aldehydes to carboxylic and dicarboxylic acids. It has been postulated that similar reaction pathways also occur in the atmosphere (Simoneit and Mazurek, 1982, 1989; Kawamura and Gagosian, 1987; Kawamura and Kaplan, 1987).

5.5.1 Ambient n-Alkenoic Acid Concentrations—1982.

Even though a number of unsaturated fatty acids are known to be emitted into the atmosphere, only the dominant $C_{18:1}$ (oleic acid) has been identified to date in the fine particle samples taken during the present study. No palmitoleic acid (Δ^9-$C_{16:1}$) acid was identified, again indicating that the atmosphere is a likely sink for mono- and multi-unsaturated fatty acids.

At San Nicolas Island, oleic acid concentrations were below the detection limit (< 20 pg m^{-3}) during both the summer and winter seasons. Urban oleic acid concentrations of nearly 80 ng m^{-3} were measured in wintertime with the lowest oleic acid concentration of 6 ng m^{-3} observed during the summer season (Fig. 5.5.1). The normalized oleic acid/elemental carbon distribution patterns show winter maxima and extended summer minima (Fig. 5.5.1), which could be the result of enhanced atmospheric oxidation reactions during the summer sampling period.

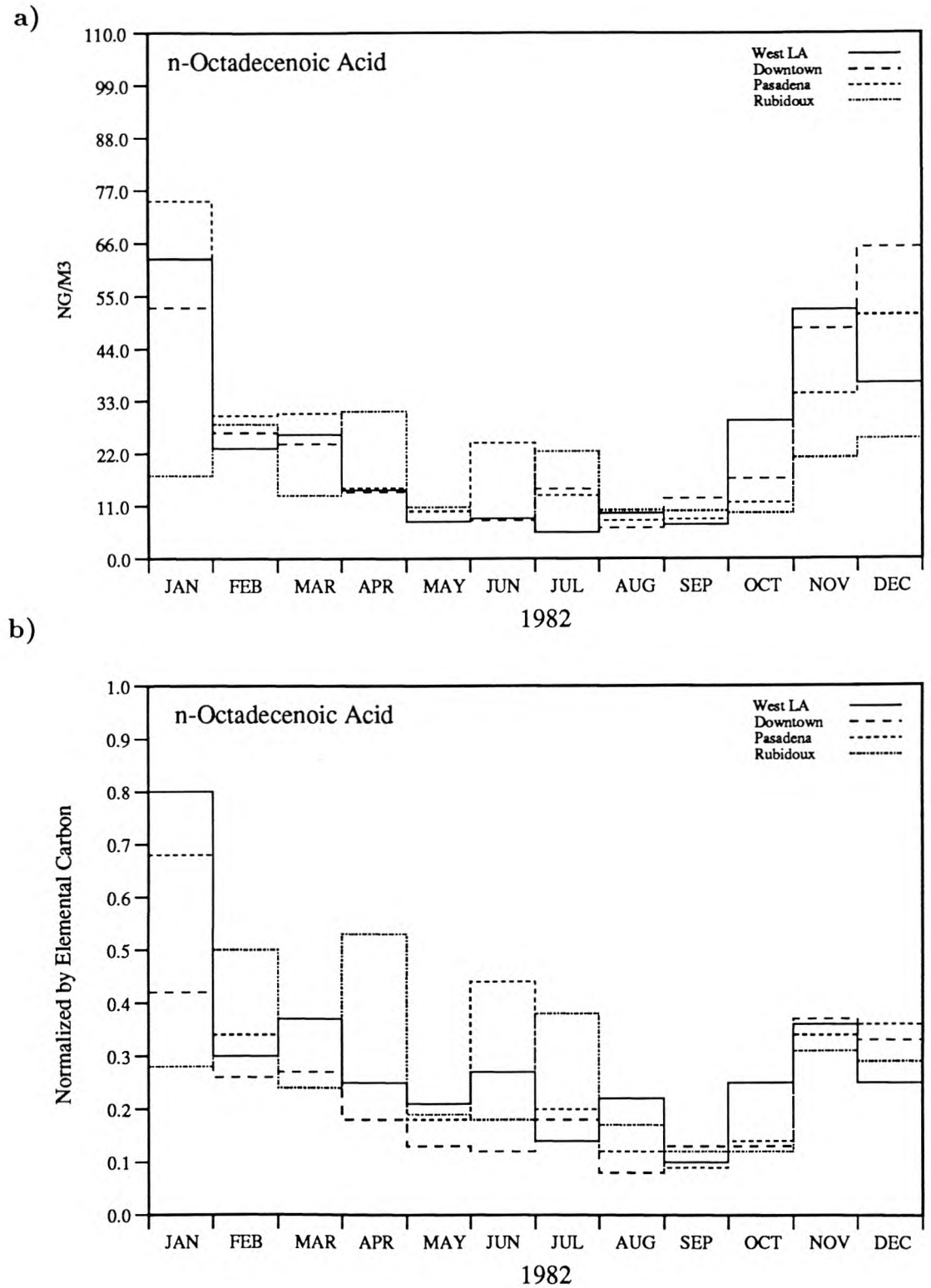

Fig. 5.5.1 Oleic acid ($C_{18:1}$): a) monthly averaged ambient concentration profiles b) monthly normalized concentration profiles.

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5.6 Normal Alkanals

In the present study, only one n-alkanal has been identified and its ambient concentration estimated. Nonanal was recently identified in fine particulate matter coming from meat cooking operations (Rogge et al., 1991). It is also the most commonly observed aliphatic aldehyde found in cooked meat (Baines and Mlotkiewicz, 1983). In meat science, n-alkanals are considered to be autoxidation products of unsaturated fatty acids. The most common unsaturated fatty acids in animal and vegetable oils and also in meat fat itself are oleic and palmitoleic acid having both a Δ^9-double bond (Baines and Mlotkiewicz, 1983; Lovern, 1965). Oxidation reactions in the atmosphere, involving oleic and palmitoleic acid may lead to nonanal.

5.6.1 Ambient n-Alkanal Concentrations — 1982.

Only one n-alkanal has been quantified so far in the ambient samples: nonanal. The measured monthly average ambient concentrations of nonanal never exceeded 20 ng m^{-3} during the sampling year 1982. Interestingly, in wintertime, the concentration distributions are very similar for all urban sampling sites, while in summer, two distinct groups of sampling sites emerge: West LA and Downtown LA show slightly enhanced concentrations during early summer; in contrast, Pasadena and Rubidoux show very pronounced ambient concentrations during the entire summer (see Fig.5.6.1a). Normalization of the ambient concentrations show drastically increased emission/atmospheric production of nonanal from April until June, similar to the behavior that will be discussed shortly for aliphatic dicarboxylic acids (see Fig.5.6.1b).

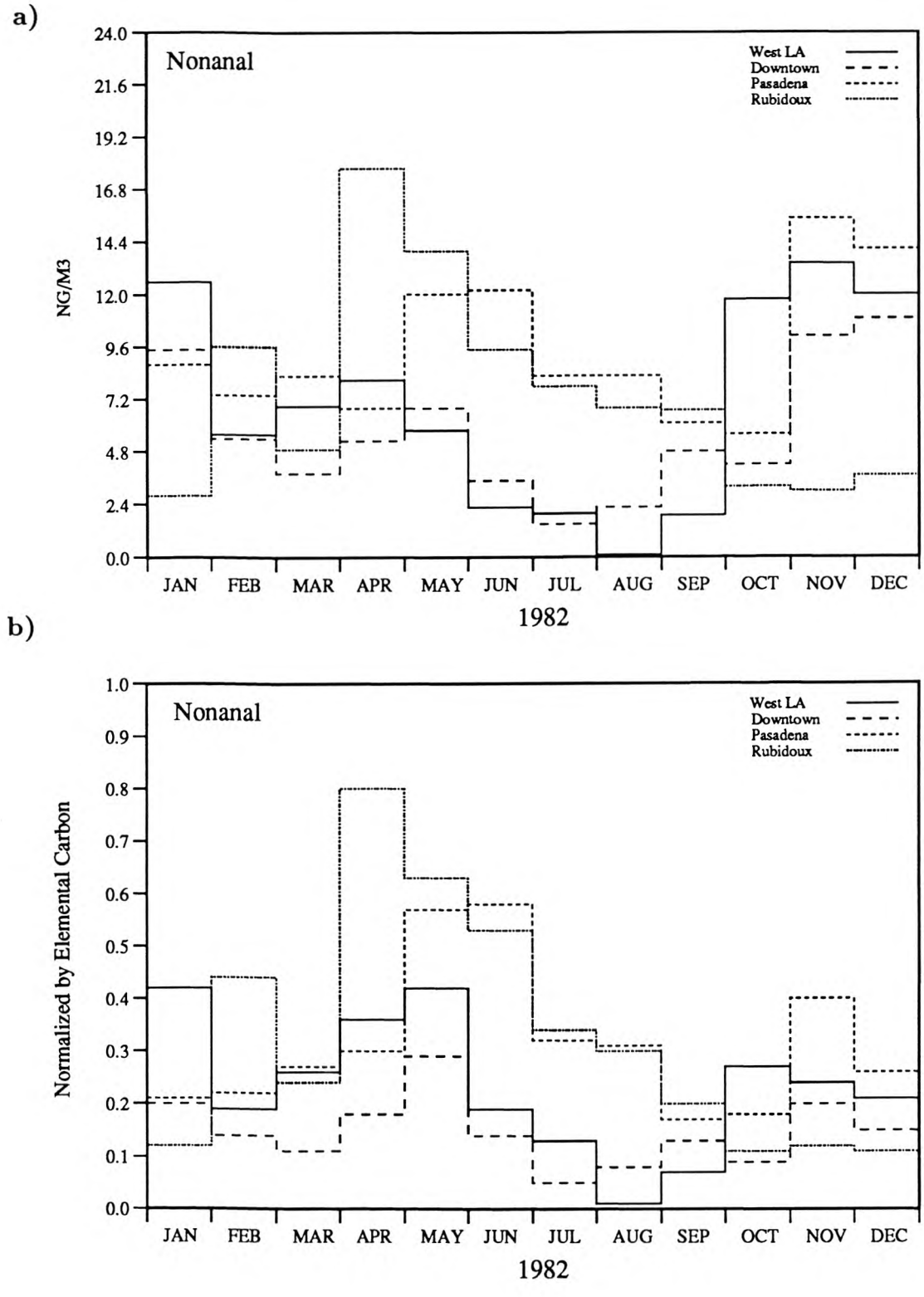

Fig. 5.6.1 Nonanal (C_9): a) monthly averaged ambient concentration profiles b) monthly normalized concentration profiles.

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5.7 Aliphatic Dicarboxylic Acids

Dicarboxylic acids found in airborne fine carbon particles constitute a very interesting compound class due to their possible formation by chemical reaction in the atmosphere (Grosjean, 1977). Airborne dicarboxylic acids ranging from C_3–C_{10} also can result from anthropogenic and biogenic emissions directly from primary aerosol emission sources (Kawamura and Kaplan, 1987; Johnstone and Plimmer, 1959; Pereira et al., 1982; Rogge et al., 1991; Simoneit, 1985).

In the past, atmospheric aliphatic dicarboxylic acid measurements generally have been made over short time periods, particularly during smog episodes (Appel et al., 1979, 1980; Cronn et al., 1977; Grosjean et al., 1978; Kawamura and Kaplan, 1987; Lunde et al., 1977; O'Brien et al., 1975; Satsumabayashi et al., 1989, 1990; Schuetzle et al., 1975; Yokouchi and Ambe, 1986). Successive short-term measurements taken for C_4–C_7 dicarboxylic acids usually reveal concentration maxima during the early afternoon (12:00–16:00), coinciding with the daily O_3 maximum (Cronn et al., 1977; Grosjean, 1977; Satsumabayashi et al., 1990). This diurnal pattern which tracks O_3 concentrations does not necessarily imply that all of the aliphatic dicarboxylic acids in the atmosphere have to be the final products of atmospheric gas phase reactions, especially since the diurnal patterns of primary n-alkanes show similar daily maxima (Appel et al., 1979; Cronn et al., 1977).

Many dicarboxylic acids demonstrate very low vapor pressures suitable for producing secondary aerosol in the atmosphere (Grosjean, 1977; Grosjean and Seinfeld, 1989; Tao and McMurry, 1989). In view of the potential for producing secondary aerosol, a number of smog chamber experiments have been conducted to identify gaseous precursor compounds, reaction mechanisms, and reaction rates for reactions that lead to linear, branched, and substituted dicarboxylic acids (Grosjean, 1977; Hatakeyama et al., 1985, 1987).

It is also postulated that atmospheric oxidation of oleic and palmitoleic acids (double bond at Δ^9) contributes to the dicarboxylic acid production in the atmosphere (Kawamura and Gagosian, 1987; Simoneit and Mazurek, 1982, 1989). Experiments with oleic acid as its methyl ester homolog and ozone in the liquid

phase have demonstrated that aldehydes, carboxylic acids and dicarboxylic acids form the final reaction products (Killops, 1986). The major reaction products were the C_9-aldehyde (nonanal), C_9-ester-aldehyde (9-oxononanoate), and C_9-acid (nonanoic acid), depending on the ozone concentrations used. Increasing the ozone concentration produced a higher yield of dicarboxylic acids, basically resulting from the more extensive oxidation of the aldehyde functional groups in precursor compounds. The extent to which results from liquid phase chemistry studies can be applied to the atmospheric aerosol is not yet clear. Experimental investigation of the heterogeneous chemistry of the ozone, oleic, and palmitoleic acids system could be used to elucidate the fate of these unsaturated acids and their reaction products.

The direct emission of aliphatic dicarboxylic acids from aerosol sources has not been extensively investigated in the past. Kawamura and Kaplan (1987) report that lower dicarboxylic acids ($\leq C_5$) were found only to a minor degree in the airborne particles collected in a greenhouse, suggesting that biogenic sources contribute only to a limited extent to the observed ambient concentrations. The 1980 Mount St. Helens volcanic eruption in conjunction with a hot, lateral blast devastating a large forest area showed that the pyrolysis of plants, trees, and organic soil consitutents results in a large number of organic compounds in airborne ash including aliphatic dicarboxylic acids ranging from C_4 to C_9 (Pereira et al., 1982). Meat cooking is another, recently investigated source for the direct emission of C_4–C_8 dicarboxylic acids, with the highest emission rates for hexanedioic acid (adipic acid) (Rogge et al., 1991). Another known source of direct emissions of these compounds results from cigarette smoke (Johnstone and Plimmer, 1959). Dicarboxylic acids ranging from C_4–C_{10} have been identified in gasoline and diesel engine exhaust (Kawamura and Kaplan, 1987). The highest emission rates were found for oxalic acid ($C_2H_2O_4$), which under normal ambient conditions is found in the vapor phase. The highest emissions of particle-bound diacids originating from gasoline combustion engines was found for methylmaleic acid (2-methyl-2-Z-butenedioic acid), followed by succinic acid (butanedioic acid) and maleic acid (2-Z-butenedioic acid). For diesel exhaust, the highest particle phase emissions were found for maleic acid, methylmaleic acid, and succinic acid. Which of the two types of combustion engines emits greater quantities of dicarboxylic acids can-

not be ascertained from the study by Kawamura and Kaplan (1987), since the experiments were of a semi-quantitative nature.

5.7.1 Ambient Dicarboxylic Acid Concentrations—1982.

The major identified dicarboxylic acids found in fine carbon particles—collected at the four urban sites—range from C_3-C_9, including branched and substituted dicarboxylic acids. At San Nicolas Island, all dicarboxylic acid concentrations were below the detection limit of 0.02 ng m^{-3} for the present study. In the urban atmosphere the following, 6 linear, 2 branched, 1 unsaturated, and 1 substituted dicarboxylic acids were identified as the dominant species:

linear:	Propanedioic acid	(malonic acid)	DF3
	Butanedioic acid	(succinic acid)	DF4
	Pentanedioic acid	(glutaric acid)	DF5
	Hexanedioic acid	(adipic acid)	DF6
	Octanedioic acid	(suberic acid)	DF8
	Nonanedioic acid	(azelaic acid)	DF9
branched:	Methylbutanedioic acid	(methylsuccinic acid)	DF4M
	Methylpentanedioic acid	(methylglutaric acid)	DF5M
unsaturated:	2-Butenedioic acid	(fumaric acid)	2DF4
substituted:	Hydroxybutanedioic acid	(hydroxysuccinic acid)	DF4H

The monthly averaged concentration profiles (1982) for C_3–C_6 dicarboxylic acids reveal more or less the same pattern for all four urban sites: high ambient concentrations from April until August, and often also for February 1982. This contrasts with the concentration profiles for n-alkanes and n-alkanoic acids, which peak during the winter months (see Figures 5.7.1a-c). Azelaic acid (DF9) shows a different seasonal distribution pattern with low summer and higher winter concentrations, except for West Los Angeles, which showed higher concentrations in late spring and early summer (Fig. 5.7.1b). The highest total dicarboxylic acid concentration was found at Rubidoux, the farthest downwind site with 580 ng m^{-3}

in June. The lowest total concentration was found at West Los Angeles during the month of September with 63.5 ng m^{-3} (Fig. 5.7.1c). Additional figures and concentration data can be found in Appendices A4 and B4. In Fig. 5.7.2, the ambient concentrations for single dicarboxylic acids are shown as a function of the lowest (September to December) and highest (April to August) concentration periods during 1982. The graphs reveal that the ambient concentration levels differ by two-fold to four-fold between these two peroids. The highest dicarboxylic acid concentrations are found for succinic acid (DF4), followed by malonic (DF3) and glutaric acid (DF5).

Ambient dicarboxylic acid concentrations normalized by elemental carbon concentrations reflect even more drastically the pattern that can be seen in most of the ambient concentration profiles: very high dicarboxylic acid inputs into the atmosphere from April until August and often even during February 1982 (Figures 5.7.3a-c). Nonanedioic acid (azelaic acid) reveals the most interesting normalized atmospheric concentration pattern. At West Los Angeles, the highest atmospheric loadings occur from April to August (peak in June), as for all the other dicarboxylic acids. But at Downtown Los Angeles and Pasadena the normalized concentrations suggest nearly constant atmospheric burden (emissions + atmospheric formation) during the entire year. At Rubidoux, the normalized azelaic acid burden is highest in wintertime. Azelaic acid is a potential atmospheric reaction product of aerosol phase palmitoleic and oleic acid emissions (both have the double bond at Δ^9), and thus may have a source that differs greatly from the other lower molecular weight dicarboxylic acids.

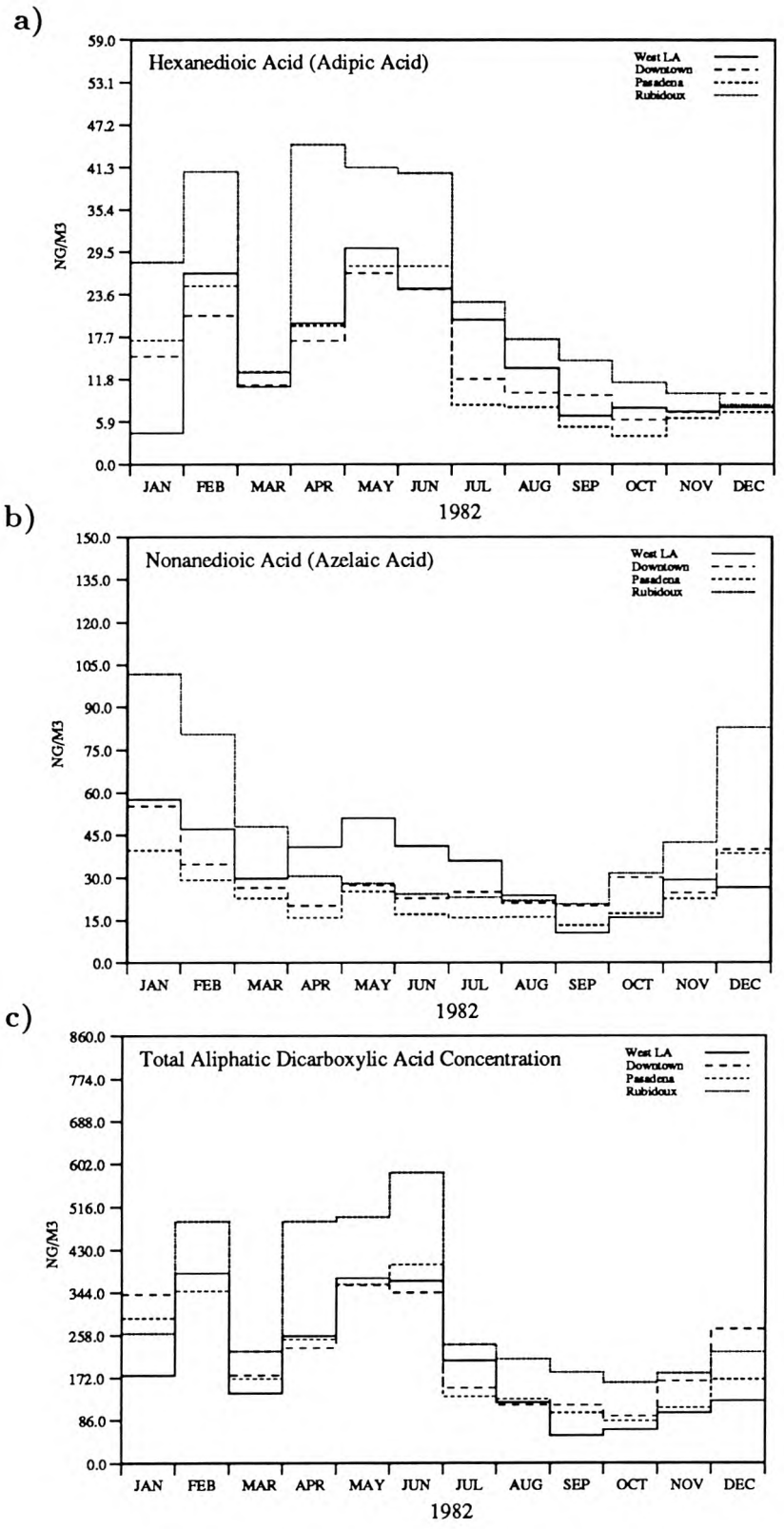

Fig. 5.7.1 Monthly averaged concentration profiles for a) hexanedioic acid, b) nonanedioic acid, and c) total aliphatic dicarboxylic acids.

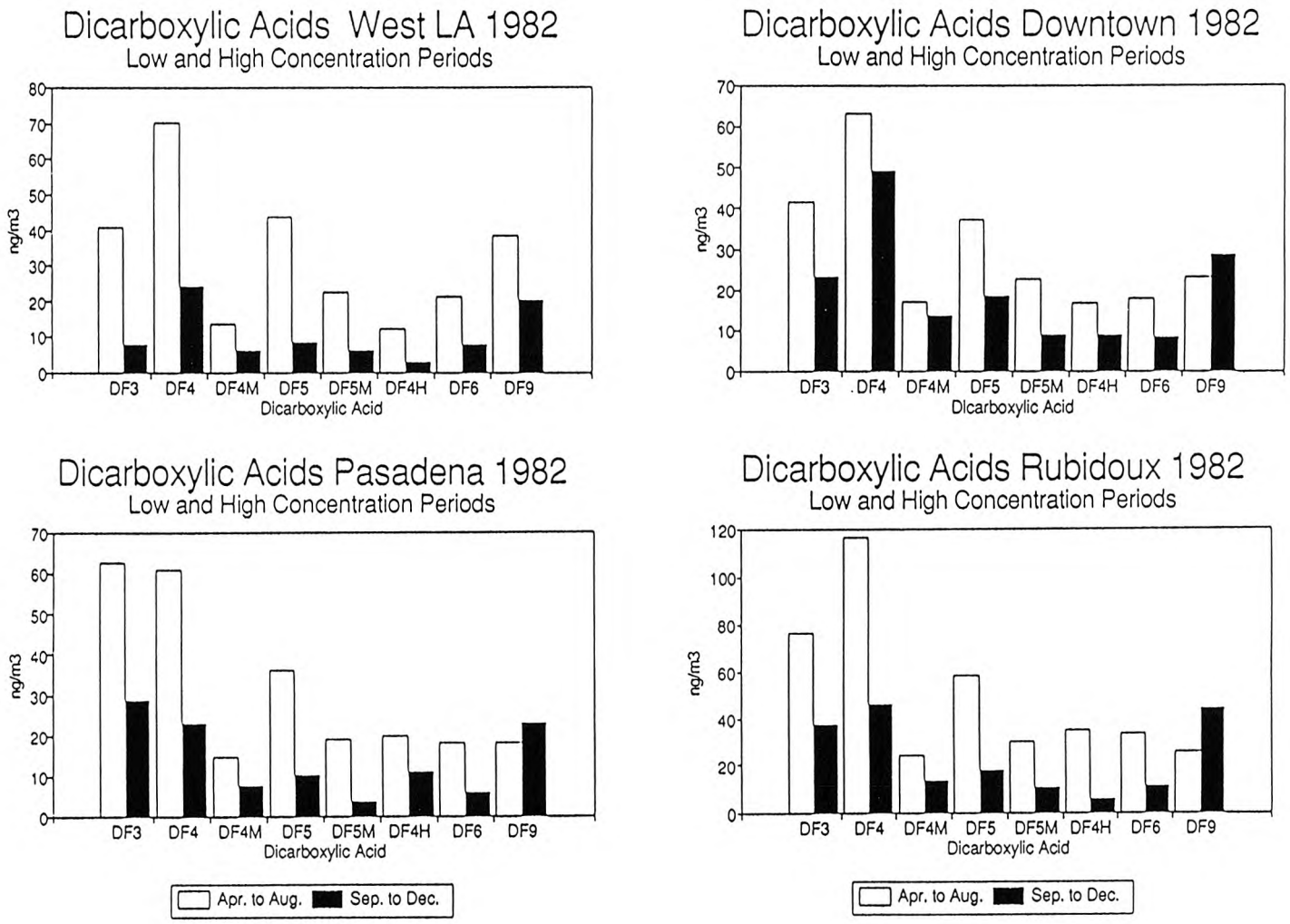

Fig. 5.7.2 Monthly averaged ambient dicarboxylic acid concentrations for low (Sep. - Dec.) and high (April - August) concentration seasons—1982.

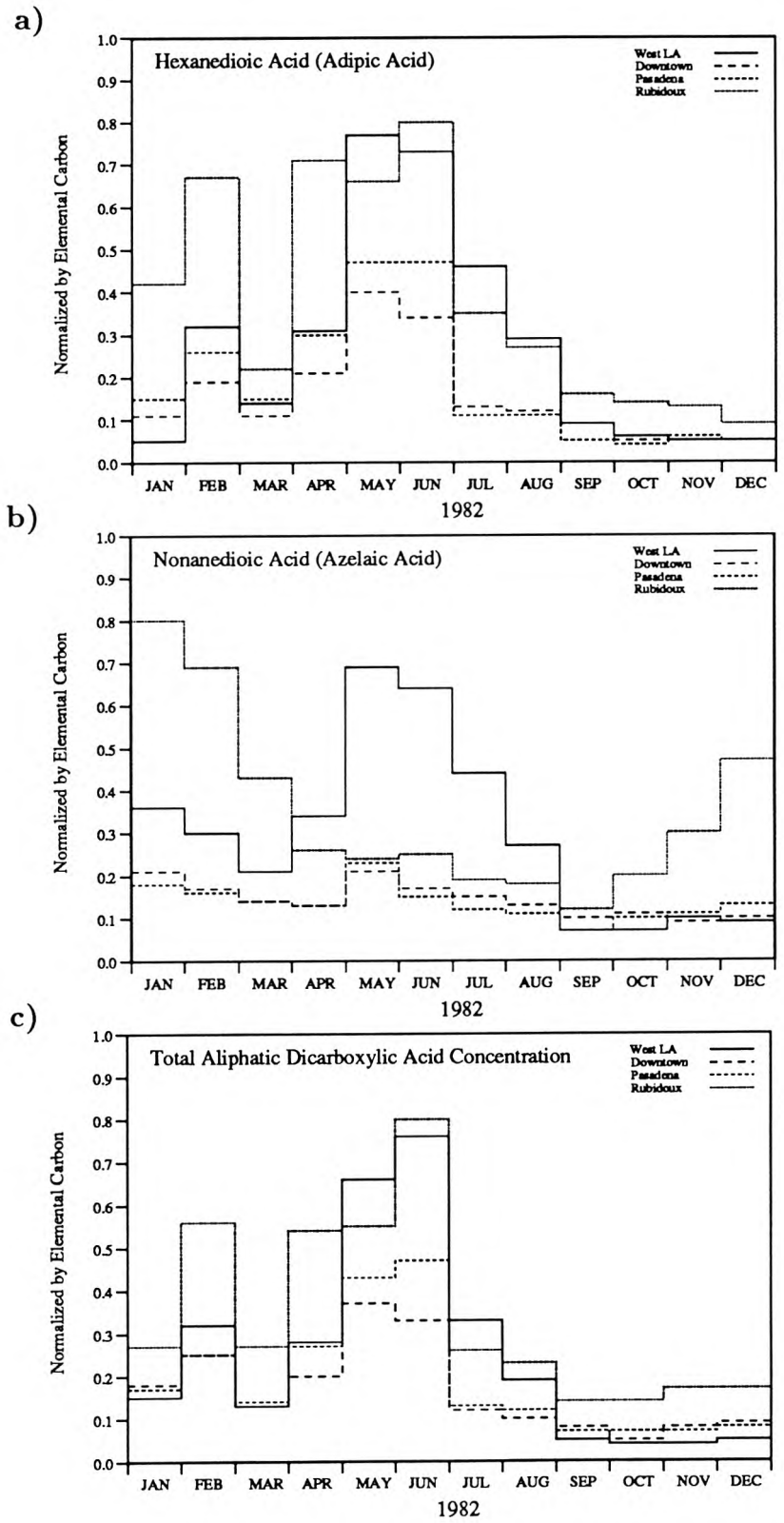

Fig. 5.7.3 Monthly normalized concentration profiles for a) hexanedioic acid, b) nonanedioic acid, and c) total aliphatic dicarboxylic acids.

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5.8 Diterpenoid Acids and Retene

Cyclic unsaturated diterpenoids together with monoterpenoids and sesquiterpenoids are natural constituents of trees, fresh cut wood and bleed resins. In temperate climates (e.g., northern industrialized hemisphere), the dominant resinous woods are related to conifereous trees (e.g., pine and spruce) and to a lesser degree to deciduous (angiosperm) trees like oak and birch. In contrast, angiosperms are the prolific resin producers in the tropical zones (Gough, 1964; Kato and Kitahara, 1978; Thomas, 1970; Simoneit, 1977). During the aging process of resins and resinous wood, the more volatile monoterpenoids and sesquiterpenoids are lost to the atmosphere; whereas, the non-volatile diterpenoids are effectively trapped. Burning lumber and the deterioration of dead wood are the major processes involved in redistributing and chemically altering the non-volatile resinous compounds (Standley and Simoneit, 1987, 1990). Amber, a fossil resin agglomerate, is found world-wide in coal, soil, and even in sedimentary rocks (Simoneit et al., 1985). Diterpenoids also have been identified in deep-sea sediments (Simoneit, 1977), and the most abundant diterpenoids are of abietic type with dehydroabietic acid as the major component. Retene, a polycyclic aromatic hydrocarbon—the complete dehydration and carboxylation product of abietic and pimaric acids—has also been identified in deep-sea sediments, either pointing towards disproportion reactions yielding retene as a final product of the geological diagenesis or towards combustion of wood as the production mechanism. Simoneit et al. (1985) examined contemporary bleed resins from Douglas fir and to disclose possible transformations also soil samples taken under a fir tree. In both cases, dehydroditerpenoids and traces of retene were found with an slight increase in unsaturation in the soil samples.

The combustion of wood and ligneous products is considered to be the most relevant input mechanism for resinous organic compounds into the accumulation mode of suspended airborne particles, including diterpenoids, phenols, PAH's, and many other natural and thermally modified natural compounds (Hawthorne et al., 1988; Ramdahl, 1983a, 1983b; Simoneit and Mazurek, 1982; Standley and Simoneit, 1987, 1990). Useful tracer compounds previously identified in ambient fine

carbonaceous particles originating from resinous wood combustion are dehydroabietic, isopimaric, and pimaric acids. Recently, controlled and quantitative wood burning experiments were conducted, using a residential fireplace (Hildemann et al., 1991a, 1991b; Mazurek et al., 1990). Oak and pine, the major firewoods burned in California homes were used. Wood combustion aerosol was collected with a dilution sampler, to simulate the atmospheric cooling, dilution, and condensation of hot stack gases onto preexisting particles that would occur as the plume disperses in the atmosphere (Hildemann et al., 1989). Interestingly, the combustion of pine wood resulted in an emission rate for dehydroabietic and isopimaric acids that was 30 times higher than was found for oak wood combustion, in good agreement with the observation that angiosperms in the northern hemisphere are minor resin producers. Although retene is expected to be an endproduct of the aromatization and decarboxylation process ongoing during the combustion process, it was detected only in minor amounts in the Los Angeles area fireplace tests conducted by Hildemann et al. (1991a, 1991b). Ramdahl (1983a) has shown that the retene-yield from wood combustion is a strong function of combustion air supply and temperature. Burning spruce wood under lean air conditions increased the retene concentration in the effluent gases by more than 500 fold compared to burning conditions at higher temperature and excess air. Space heating with a traditional open fireplace provides enough excess air to suppress the reductive conditions necessary for retene formation (Hildemann et al., 1991b; Simoneit, 1977; Simoneit et al., 1985). In cities, where 50% or more of all households use wood for space heating, ambient dehydroabietic acid concentrations have been measured and were found to range from 48 ng m^{-3} to 440 ng m^{-3} (Standley and Simoneit, 1990) and retene concentrations from 6 to 8 ng m^{-3} (Ramdahl, 1983a).

5.8.1 Ambient Diterpenoid Acids and Retene Concentrations 1982.

Although retene (1-methyl-7-isopropylphenanthrene) is a polycyclic aromatic hydrocarbon (PAH) and should be listed as such, it will be discussed together with the diterpenoid acids in order to provide a consolidated discussion of these interrelated wood smoke components.

The annual concentration pattern for the 7 identified diterpenoid acids and retene is shown in Figure 5.8.1a. Concentration changes closely follow the heating season, with highest concentrations during January, November, and December. For example, in winter, dehydroabietic acid concentrations reach 60 - 110 ng m^{-3}, while from February until April the dehydroabietic acid concentrations abruptly decline to about 28 ng m^{-3} (Fig.5.8.1b). During the summer, the ambient concentrations were around 1.0 ng m^{-3} and lower, indicating little or no emissions due to wood combustion. Retene, the fully aromatized product from the pyrolysis of abietic and pimaric type compounds shows maximum concentrations of only 0.55 ng m^{-3} during the heating season. At San Nicolas Island, none of the wood smoke compounds could be detected. Additional annual concentration profiles are available in Appendices A6 and B6.

The following table summarizes the results for the wood smoke constituents found in ambient fine particulate samples:

Table 5.8.1 Maximum Wintertime Concentrations of Wood Smoke Markers in Ambient Air—Los Angeles area, 1982

Compound Name	max. Winter[a] Concentration ng m^{-3}	max. Annual Average[b] Concentration ng m^{-3}
Dehydroabietic Acid	107.3	23.6
7-Oxodehydroabietic Acid	14.1	4.1
Pimaric Acid	18.6	4.8
Isopimaric Acid	10.3	2.3
8,15-Pimaradien-18-ic Acid	5.5	1.1
Sandaracopimaric Acid	9.1	2.2
13-Isoproyl-5α-podocarpa-6,8,11,13-tetraen-16-oic Acid	5.2	1.2
Retene	0.55	0.10[c]

[a] Highest monthly average value measured at any of the monitoring sites studied.

[b] Highest annual average value at any of the monitoring sites studied.

[c] Retene was only detected during the heating season; therefore, the annual average value is very low.

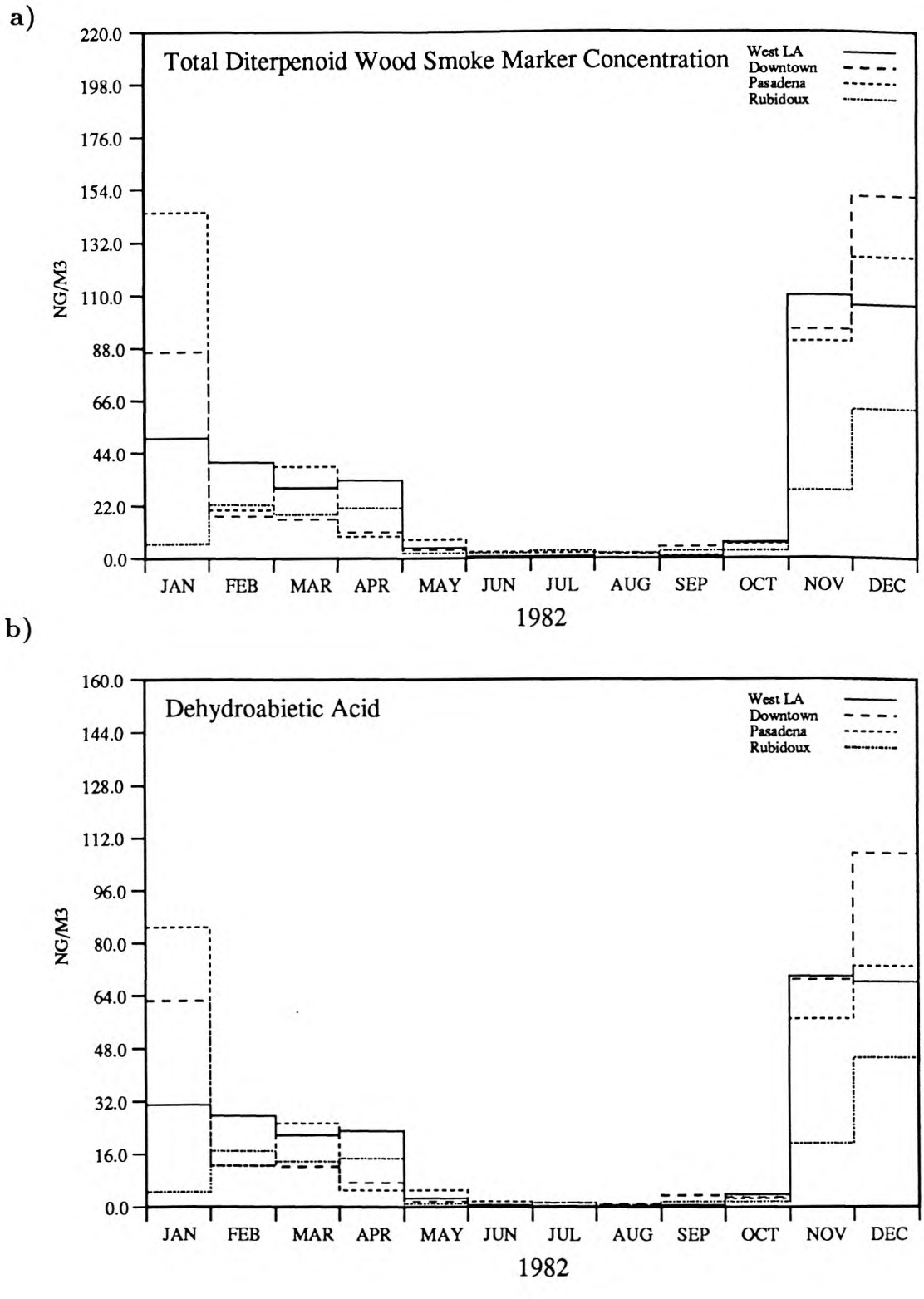

Fig. 5.8.1 Monthly averaged concentration profiles for a) total diterpenoid wood smoke markers including retene and b) dehydroabietic acid.

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5.9 Aromatic Polycarboxylic Acids

Aromatic acids are comprised of the benzoic and naphthoic acid types as well as similar compounds that have additional substituents on the aromatic ring system (ranging from methyl groups to hydroxy, methoxy, and carboxyl groups). Hydroxy substituted benzoic acids and aromatic di- and tricarboxylic acids have been reported in airborne particulate samples (Cautreels and Van Cauwenberghe, 1976; Matsumoto and Hanya, 1980; Satsumabayashi et al., 1989; Simoneit, 1986; Wauters et al., 1979; Yokouchi and Ambe, 1986) and also in the rainwater of urbanized areas (Kawamura and Kaplan, 1983; Simoneit and Mazurek, 1989). Mono- and polyhydroxy substituted benzoic acids (or methoxy and polymethoxy acids) are believed to be mainly of biogenic origin, e.g., from vascular plants, pollen, fungi, and bacteria (El-Basyouni et al., 1964; Hillis and Inoue, 1968; Ratledge, 1964; Smith, 1955; Strohl and Seikel, 1965). Naphthoic acids have not yet been detected in aerosols. In the present study, relatively abundant aromatic di-, tri- and tetracarboxylic acid compounds, for which authentic standards are available, will be discussed. A search for phenolic acids and other compounds in this class will be conducted later when the authentic standard compounds needed to confirm such identifications have been obtained.

Some aromatic acid emissions to the atmosphere are thought to arise from biogenic or human-influenced natural sources. Kawamura and Kaplan (1987) reported that phthalic acid (1,2-benzenedicarboxylic acid) and methylphthalic acids were found in suspended particles collected in a greenhouse. However, the concentrations measured inside the greenhouse were far below the usual outdoor concentrations, suggesting that plants are not the sole source responsible for the concentrations found in ambient air. Because greenhouses are not completely sealed against outdoor air, the measured indoor trace concentrations could have originated from the outdoor atmosphere. Airborne soil dust also could contribute aromatic acids to the atmospheric fine particle complex. Soil samples have been analyzed, revealing that of the dicarboxylic acids found, phthalic acid is the second most abundant diacid after oxalic acid. Kawamura and Kaplan (1987) argue that phthalic and methylphthalic acid in soils may be the degradation products of lignin-type ma-

terial metabolized by microorganisms. Since the soil samples discussed here were taken in West Los Angeles, it is possible that the soil samples reflect contributions from urban dry deposition of dust, which also contains large amounts of phthalic acids (Kawamura and Kaplan, 1987). Phthalic acids have been isolated in poppies, cranberries, and even in tobacco smoke (Graham, 1973; Johnstone and Plimmer, 1959). Interestingly, phthalic acid has been identified in tobacco smoke but not in tobacco leaves, indicating possible phthalic acid production during cigarette combustion (Johnstone and Plimmer, 1959).

Besides the natural occurrence of aromatic polycarboxylic acids, phthalic and methylphthalic acids have been identified in particulate automobile exhaust emissions (Kawamura and Kaplan, 1987; Simoneit, 1985). Although the source testing procedures used were of a semiquantitative nature, the emission rates for phthalic acids from a diesel automobile exceeded the emissions from a gasoline powered car by more than tenfold (Kawamura and Kaplan, 1987). It was suggested that 1,2-benzenedicarboxylic acids and their methyl substituted homologs can be formed as the incomplete combustion products of naphthalenes (Kawamura and Kaplan, 1987).

Another possible source for phthalic acids is the industrial production of phthalate esters (ester R = $(CH_2)_n$–CH_3 n =1 to 7) which are used in enormous amounts as plasticizers in the production of plastics (about 500,000 kg were manufactured in 1972 (Graham, 1973)). The technical production of phthalates starts with the catalytic oxidation of either naphthalene or o–xylene (using V_2O_5 as promoter) to yield phthalic anhydride, which is the precursor compound used for the production of phthalates (Graham, 1973). The industrial esterification of phthalic anhydride employs different types of alcohols (depending on the plasticizer type wanted) promoted by p-toluene-sulfonic acid. Graham (1973) reported that the industrial process yield for the first step is above 99.5% phthalic anhydride, the rest is made up of phthalic acid, isophthalic acid, terephthalic acid, and malic anhydride. The purity of the manufactured esters ranges from 99.7% to 99.97%. One possible route for creation of airborne phthalic acids may involve the aging of plastic material in the environment. The attack of water molecules on the functional

ester groups (hydrolysis) can result in the formation of the parent phthalic acid (Allara, 1975). Applied to atmospheric chemistry, it may be plausible that airborne phthalate esters hydrolyze forming phthalic acid (Kawamura and Kaplan, 1983). For hydrolysis, it is necessary that either acid or base catalysis occurs (Allara, 1975), which could be provided by the atmospheric aqueous sulfur and/or nitrogen chemistry or other suitable airborne agents. Phthalates also are susceptible to direct photolysis ($\lambda \geq 290$nm) and hydroxyl radical attack (Howard, 1989; Atkinson, 1987). For the time being it can only be speculated how effective the hydroysis of plasticizers in the atmospheric gas and particle phase could be, especially when compared to competitive photolysis and hydroxyl radical chemistry.

Phthalic acid and related compounds also could be produced by atmospheric chemical reactions involving directly emitted PAH's. Grosjean et al. (1987) conducted several experiments to elucidate the ozone reaction mechanism for the colorants alizarin and alizarin crimson (calcium-aluminum lake of alizarin). Interestingly, the most prominent degradation product of these anthraquinone derived compounds was found to be phthalic acid. Moriconi et al. (1961) and Moriconi and Taranko (1963) investigated reactions of benzo[a]pyrene and of 3-methylcholanthrene with ozone in CH_2Cl_2 and CH_2Cl_2-MeOH. They concluded that the test PAHs were converted via polycyclic aromatic quinones (PAQ's) into polycarboxylic aromatic acids (ring-opening products), including aromatic di-, tri-, and tetracarboxylic acids. Thus it may be speculated that ambient ozone-PAH reactions could lead via PAQ's as intermediates to polycarboxylic aromatic acids as major degradation products.

Up to the present time only Wauters et al. (1979) have reported the finding of benzenetricarboxylic acids in airborne particulate matter. In addition, there exists presently no evidence that benzenetri- or benzenetetracarboxylic acids are emitted due to primary anthropogenic or biogenic activities.

5.9.1 Ambient Aromatic Acid Concentrations—1982.

Eight aromatic di-, tri and tetracarboxylic acids were identified in the ambient fine particulate matter samples collected at the four urban sites in the Los Angeles

area. None of the aromatic acids mentioned here could be found at our remote station on San Nicolas Island. The major aromatic acid found in airborne fine particles was phthalic acid with peak monthly averaged ambient concentrations of up to 120 ng m^{-3}, followed by trimesic acid and 4-methylphthalic acid, each showing monthly averaged ambient concentrations of up to 50 ng m^{-3} during summertime. The identified aromatic acids are listed in Table 5.9.1. All aromatic acids except isophthalic and terephthalic acid show highest concentrations from May to July 1982, with high concentrations also in February 1982. The seasonal concentration profiles for phthalic, trimesic, and pyromellitic acids are shown in Fig.5.9.1a-c, and are seen to closely resemble the annual aliphatic dicarboxylic acid concentration profiles (cf. Chap. 5.7), indicating that aromatic di-, tri-, and tetracarboxylic acids may well be dominated by the products of atmospheric chemical reactions as discussed above.

Normalizing the ambient aromatic acid concentrations by elemental carbon concentrations demonstrates even more drastically that the aromatic acid formation/release preferentially occured during the late spring and early summer as well as in February-1982. Concentration profiles for the remaining aromatic acids studied are given in Appendices A7 and B7.

Table 5.9.1 Aromatic acids identified in ambient fine particles—1982

Compound Name	
1,2-Benzenedicarboxylic acid	(phthalic acid)
1,3-Benzenedicarboxylic acid	(isophthalic acid)
1,4-Benzenedicarboxylic acid	(terephthalic acid)
4-Methyl-1,2-benzenedicarboxylic acid	(4-methylphthalic acid)
1,2,3- and 1,2,4-Benzenetricarboxylic acid	(hemimellitic and trimellitic acid)[a]
1,3,5-Benzenetricarboxylic acid	(trimesic acid)
1,2,4,5-Benzenetetracarboxylic acid	(pyromellitic acid)

[a] Hemimellitic and trimellitic acid have the same GC-retention time and similar spectra; hence, they are reported together.

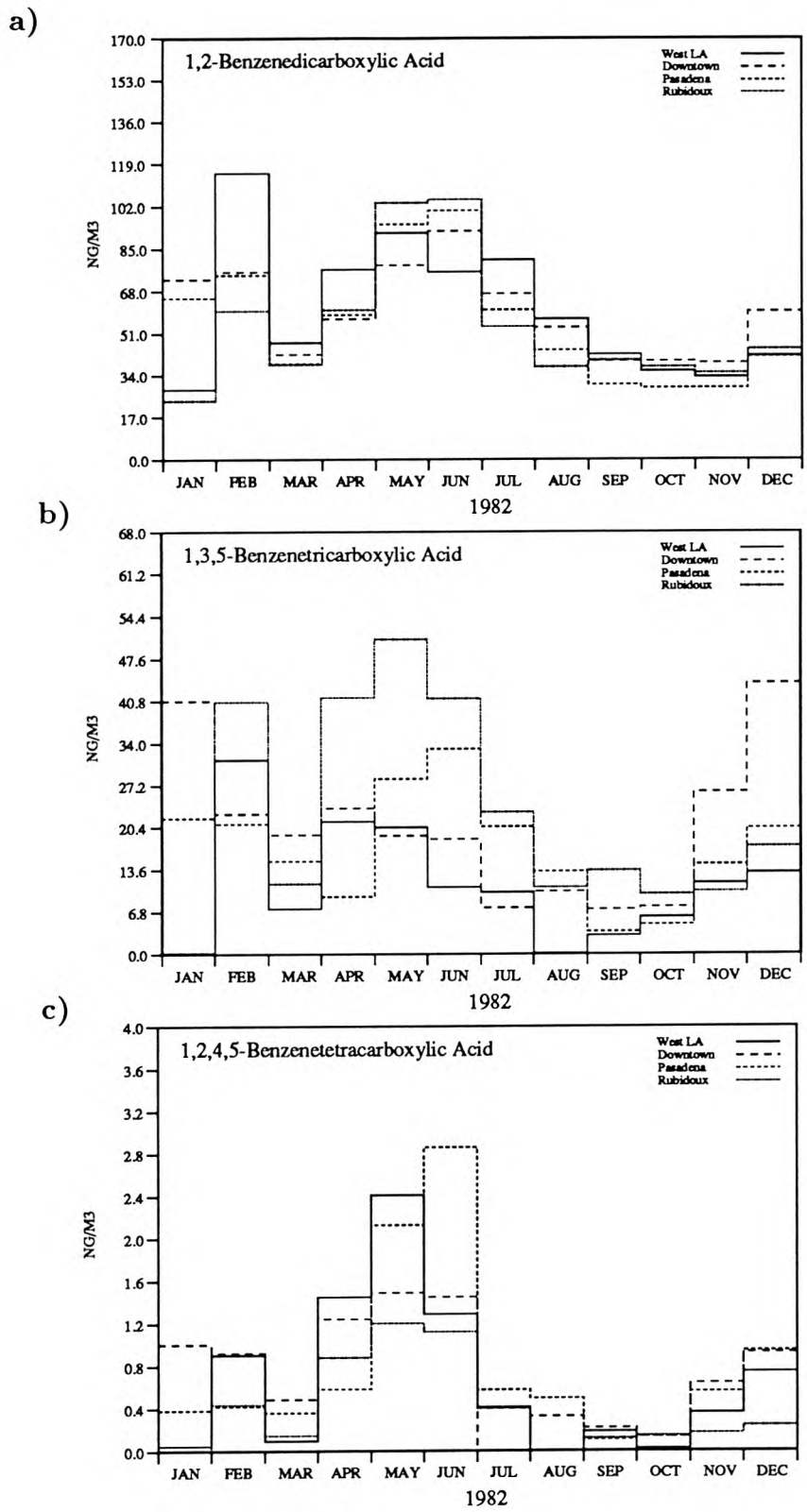

Fig. 5.9.1 Monthly averaged concentration profiles for a) 1,2-benzenedicarboxylic acid, b) 1,3,5-benzenetricarboxylic acid, and c) 1,2,4,5-benzenetetracarboxylic acid.

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5.10 Polycyclic Aromatic Hydrocarbons

Due to their mutagenic and carcinogenic potential, polycyclic aromatic hydrocarbons (PAH's) have been extensively investigated in the past. They are considered to be the pyrolysis products of incomplete combustion of organic matter (Alsberg et al., 1985; Grimmer et al., 1983; Tong and Karasek, 1984). Produced during combustion processes, PAH's are introduced into the atmosphere in the fine particle mode ($\leq 2.5\mu$m) attached to fine carbon particles (Daisey et al., 1986; Miguel and Friedlander, 1978; Leuenberger et al., 1988). When exposed to O_3, NO_2, N_2O_5, and other oxidants, PAH's slowly react in the atmosphere (Brorström et al., 1983; Kamens et al., 1990; Nielson, 1988; Pitts et al., 1985).

5.10.1 Ambient Polycyclic Aromatic Hydrocarbon Concentrations —1982.

Fifteen PAH's have been identified in fine particle samples studied here, of which one is currently labeled as tentatively identified (indeno[1,2,3-cd]fluoranthene). Because chrysene and triphenylene have very similar fragmentation patterns in the mass spectrometer and coelute on the GC column used here these two PAH's will be grouped together. Since coronene elutes very late in each GC run, coronene data were taken only at West Los Angeles. The following list summarizes the PAH's quantified in ambient fine particulate matter during the present study:

Fluoranthene, pyrene, benz[a]anthracene, benzo[ghi]fluoranthene, cyclopenta-[cd]pyrene, chrysene, triphenylene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, indeno[1,2,3-cd]fluoranthene, benzo[ghi]perylene, and coronene.

The seasonal concentration patterns for all PAH's are very similar, with high winter and low summer concentrations. The highest concentrations were usually found for benzo[ghi]perylene (nearly 20 ng m^{-3}), followed by coronene (close to 10 ng m^{-3} (data only available for West LA)). The summer concentrations are usually very low and sometimes below our detection limit (10 pg m^{-3}). Fig. 5.10.1a shows as an example the annual concentration distribution pattern for benzo[ghi]-

perylene. Monthly averaged total PAH concentrations in fine particles of up to 40 ng m^{-3} and more were measured during wintertime. It is worth mentioning that the very low summer PAH concentrations reflect the increased dilution that occurs in summer, but probably also the increased degradation rate of PAH's as a result of the more active photochemistry prevailing in the atmosphere in the summer months. This can be seen in Fig. 5.10.1b where benzo[ghi]perylene concentrations have been normalized by elemental carbon concentrations in order to remove the effect of increased dilution in summer. Summer minima still are observed in the normalized seasonal pattern, indicating the presence of enhanced photochemical destruction and/or transfer of PAH's to the gas phase due to the higher ambient temperatures. Additional source emissions (e.g. from wood smoke) may also be present in winter months. Further graphs showing the seasonal concentration patterns and normalized concentrations of individual PAH's are given in Appendices A8 and B8.

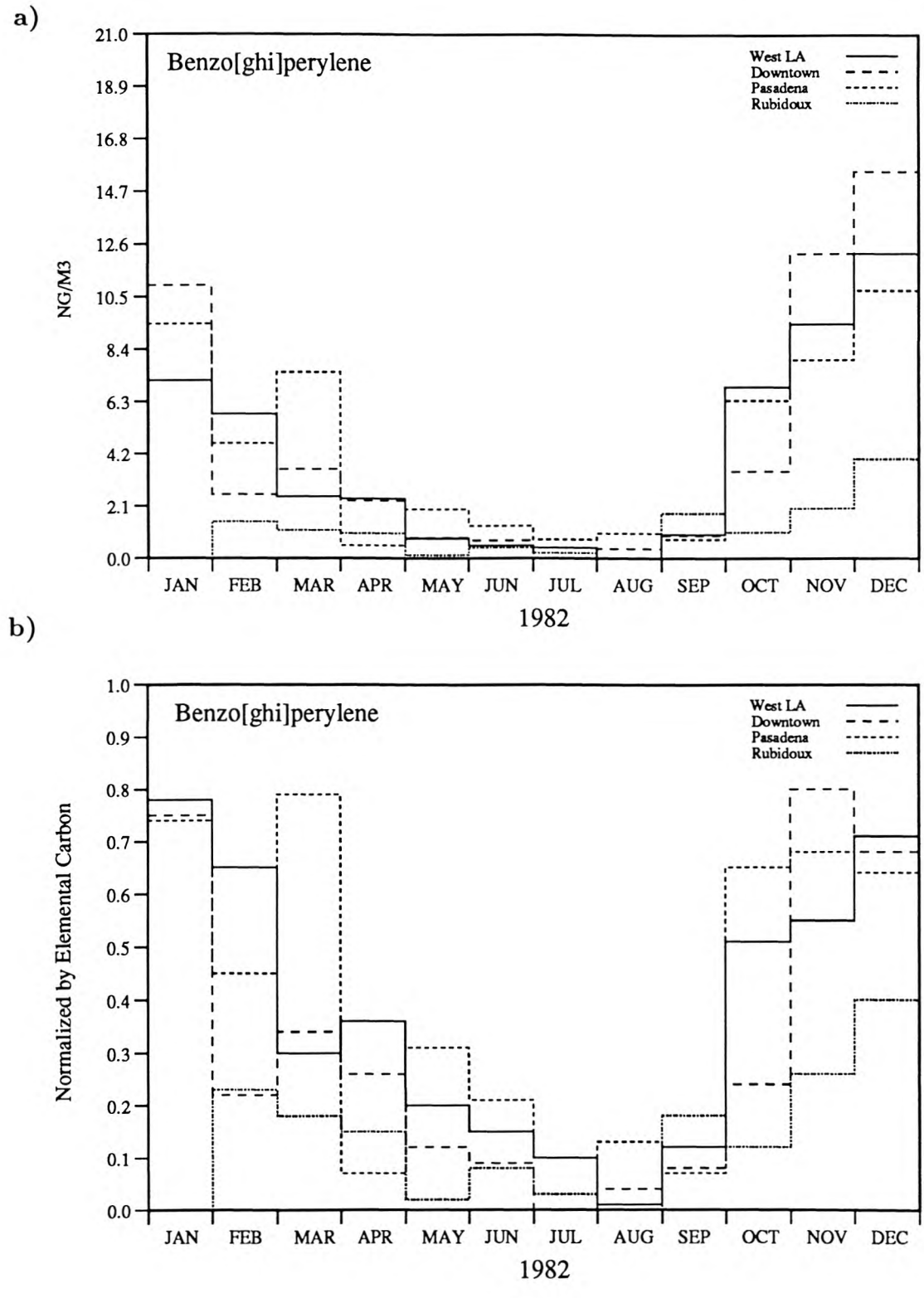

Fig. 5.10.1 Benzo[ghi]perylene: a) monthly averaged concentration profiles and b) monthly normalized concentration profiles.

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5.11 Polycyclic Aromatic Ketones and Quinones

Oxygenated polycyclic aromatic hydrocarbons found in ambient fine particulate samples are the result of primary emissions from combustion sources, atmospheric homogeneous and heterogeneous reactions and possibly chemical conversion during the sampling process itself (Schuetzle, 1983; Van Cauwenberghe et al., 1979). The extended class of oxygenated polycyclic aromatic hydrocarbons (OXY–PAH's) can be subdivided further into polycyclic aromatic ketones (PAK's), anhydrides, carboxylic acids, aldehydes, coumarins, and disubstituted polycyclic aromatic compounds such as diphenols, dialdehydes, dicarboxylic acids, and quinones (PAQ's) (Van Cauwenberghe et al., 1979).

Like PAH's, polycyclic aromatic ketones (PAK's) and polycyclic aromatic quinones (PAQ's) result either directly from combustion sources or combustion derived precursor compounds; hence, it is not surprising that they show seasonal concentration distributions in the polluted atmosphere that are similar to the PAH's (König et al., 1983; Pierce and Katz, 1976; Ramdahl and Becher, 1982; Sawicki, 1967; Stanley et al., 1969). PAK's have been identified in the particulate emissions coming from gasoline and diesel engines (Alsberg et al., 1985; Behymer and Hites, 1984; Choudhury, 1982; Jensen and Hites, 1983; Newton et al., 1982; Schuetzle, 1983; Yu and Hites, 1981) and in emissions from burning of biomass, such as wood, leaves, cereal straw, etc. (Alsberg and Stenberg, 1979; Ramdahl, 1983; Ramdahl and Becher, 1982; Sawicki et al., 1965).

Directly emitted PAK's are considered to be the transformation products of PAH's containing a single-bonded carbon atom (methylene PAH's) which oxidize immediately after leaving the reductive combustion zone (Ramdahl, 1983; Van Cauwenberghe, 1983). Another important source for PAK's and PAQ's is the photochemically induced oxidation of precursor PAH's during atmospheric transport. Khan et al. (1967) and Pitts et al. (1969) state that in particular tetracyclic and pentacyclic PAH's absorb UV solar radiation and effectively transfer their excitation energy to O_2 creating singlet molecular oxygen O_2 ($^1\Delta_g$) with which they can subsequently react, producing oxygenated PAH's. Another possible source of singlet molecular oxygen is the Hartley Photolysis (200 nm $\leq \lambda \leq$ 320 nm) of ozone in

the polluted urban atmosphere that can contribute to the PAH-oxidation (Kummler et al., 1969). An additional very important reaction pathway is the aggressive interaction of PAH's with O_3, yielding PAK's and PAQ's as were found in photooxidation experiments (Lane and Katz, 1977; Pitts et al., 1980; Van Cauwenberghe, 1983).

To investigate the possible mutagenic and carcinogenic potential of exhaust particles from gasoline powered cars, Alsberg et al. (1985) fractionated the carbonaceous particle mass into five polarity classes, ranging fron nonpolar to very polar, and performed Ames *Salmonella* mutagenicity tests on each subfraction, aryl hydrocarbon hydroxylase inducibility receptor affinity tests (AHH), and cytotoxicity tests to pulmonary alveolar macrophages (PAM). The subfractions containing most of the OXY-PAH's proved to be most potent in all three single test-types. But isolation of some of the most common low molecular weight PAK's (fluoren-9-one, phenalen-1-one, and xanthone) followed by repetition of the same tests indicated that these major compounds could not by themselves explain the enhanced potency of the complete aerosol mixture.

Epstein et al. (1968) determined the biological activity of organic subfractions of ambient organic particulate matter with *paramecium caudatum.* They concluded that 7-H-benz[de]anthracen-7-one and associated compounds show some genotoxicity. It seems likely that complex mixtures containing members of this compound class show mutagenic potential, but it remains unclear if there is a genotoxic potential for single entities or simple combinations thereof.

5.11.1 Ambient PAK and PAQ Concentrations—1982.

During this initial search for PAK's, PAQ's, and other OXY-PAH's, two PAK's and one PAQ have been identified and confirmed. It is possible that the number of positively identified OXY-PAH's could be increased if additional sets of standard compounds could be acquired for comparison against the ambient data base. So far the definitively identified OXY-PAH's are: 7H-benz[de]anthracen-7-one (benzanthrone), 6H-benzo[cd]pyren-6-one, and benz[a]anthracen-7,12-dione (1,2-benzanthraquinone). All three compounds have been identified as major OXY-PAH's in

ambient air and combustion sources (e.g., Cautreels and Van Cauwenberghe, 1976; Choudhury, 1982; König et al., 1983; Ramdahl, 1983). They exhibit enhanced winter and reduced summer concentrations, ranging from about 0.1 ng m^{-3} to more than 4.0 ng m^{-3} depending on the sampling site and compound considered (see Fig. 5.11.1a-c for more details). When normalized, 7H-benz[de]anthracen-7-one and 6H-benzo[cd]pyren-6-one concentration plots reveal pronounced winter inputs to or production in the atmosphere or enhanced destruction by atmospheric reactions in summer. When compared to the normalized PAH concentration profiles (cf. Chapter 5.10), OXY-PAH's demonstrate less pronounced summer minima, indicating that atmospheric processes in addition to combustion emissions affect the concentations measured during smog seasons, as discussed above. Benz[a]-anthracen-7,12-dione seems to have a high emission rate or atmospheric formation rate during April and May of 1982, similar to the situation found for the possibly secondary aliphatic dicarboxylic acids (see Fig. 5.11.2a-c).

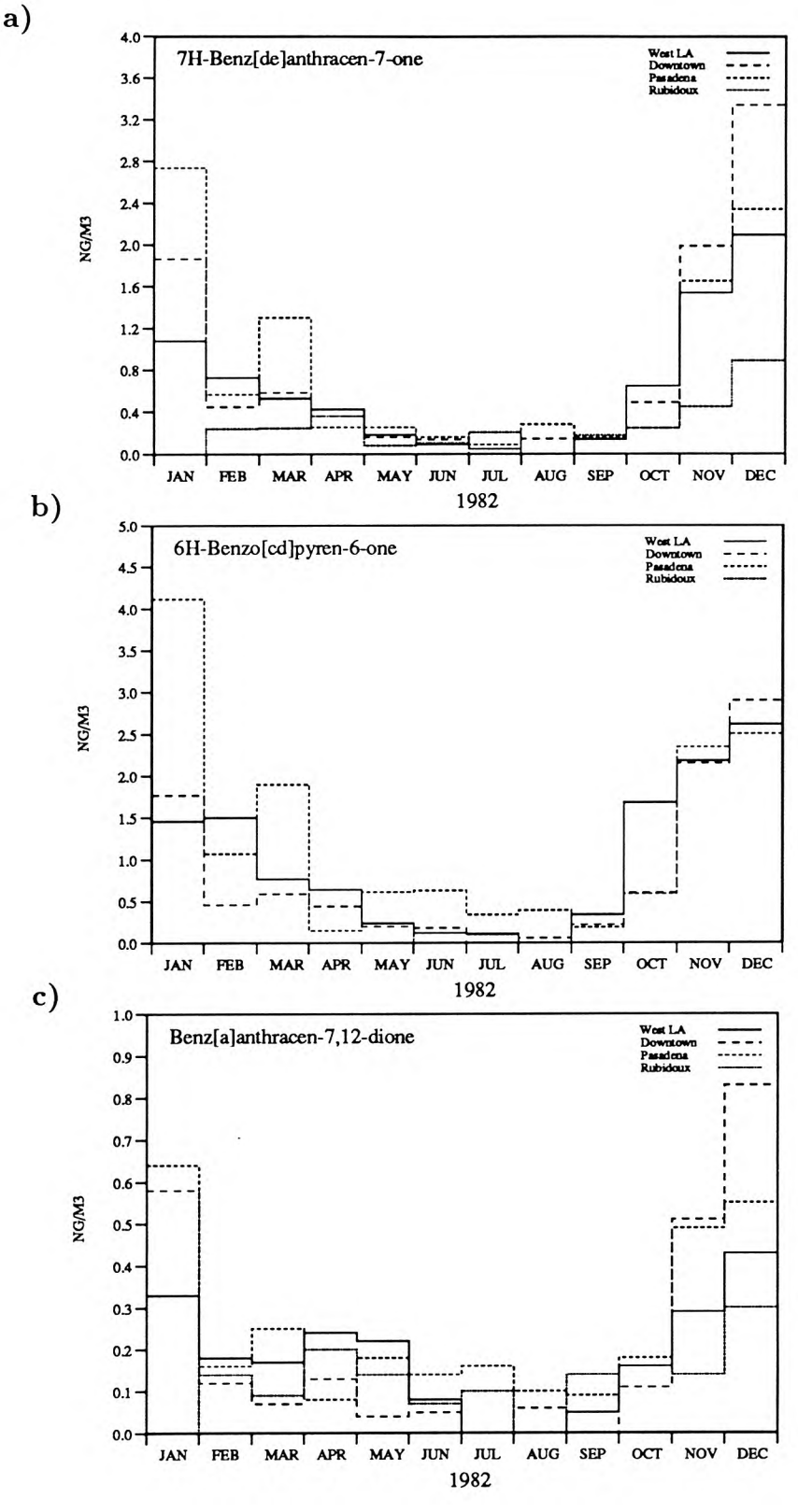

Fig. 5.11.1 Monthly averaged concentration profiles for a) 7H-benz-[de]anthracen-7-one, b) 6H-benzo[cd]pyren-6-one, and c) benz[a]anthracen-7,12-dione in LA–1982.

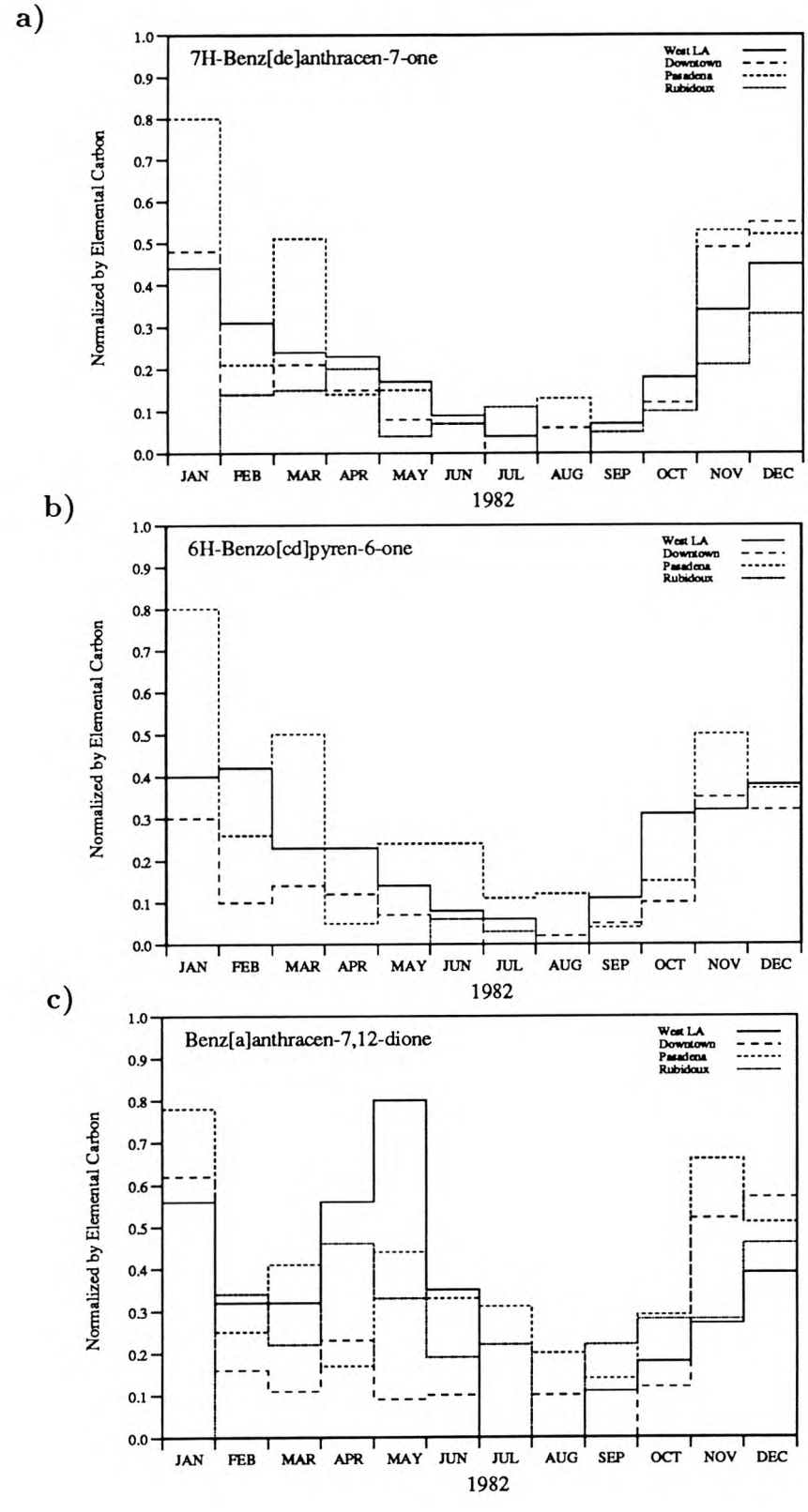

Fig. 5.11.2 Normalized concentration profiles for a) 7H-benz[de]anthracen-7-one, b) 6H-benzo[cd]pyren-6-one, and c) benz-[a]anthracen-7,12-dione in LA–1982.

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5.12 N-Containing Compounds

Four nitrogen containing compounds, having either a nitrogen atom in their functional groups or embedded in the polycyclic aromatic ring system, were positively identified: 3-methoxypyridine, 1,2-dimethoxy-4-nitro-benzene, isoquinoline, and 1-methylisoquinoline. None of them could be detected at San Nicolas Island. Concentration profiles can be seen in Appendices A10 and B10.

5.13 Summary

More than 80 single organic compounds present in the Los Angeles area fine particle complex have been quantified in terms of both temporal and spatial characteristics. Forty-eight monthly ambient filter sample sets collected at four urban sites (West Los Angeles, Downtown Los Angeles, Pasadena, and Rubidoux), representing the entire year 1982, were examined using high resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS). In addition, to evaluate background concentrations, samples taken at San Nicolas Island were analyzed by the same techniques.

Table 5.13.1 summarizes the results for all organic compounds quantified in this study. The annual average ambient concentrations for all four urban sites and average concentrations (Jul. - Dec.) for San Nicolas Island are listed. Without exception, the organic compound concentrations within the urbanized air basin are much higher than at the background site at San Nicolas Island, confirming the importance of human activities in contributing organic aerosols to the biosphere. The highest ambient fine particle concentrations for single compound classes were found for n-alkanoic acids and aliphatic dicarboxylic acids, followed by aromatic polycarboxylic acids.

Within the class of n-alkanoic acids, n-hexadecanoic acid and n-octadecanoic acid were the most prominent. The n-alkanoic acid class can be subdivided into two distinct groups: n-alkanoic acids $<$ n-C_{20} which show typical maxima in late spring/early summer, and higher n-alkanoic acids from n-C_{20} to n-C_{28} which show higher atmospheric inputs during the winter months.

Aliphatic dicarboxylic acids as a class reveal ambient monthly averaged concentration maxima of up to 600 ng m^{-3} in early summer, consistent with the input from secondary formation processes that are accelerated during the summer photochemical smog season. Focussing on the annual average concentrations found at the four urban sites, a concentration increase of about 50% can be seen in the prevailing summer downwind direction from the western portion of the Los Angeles basin towards Rubidoux in the east (199 ng m^{-3} vs. 312 ng m^{-3}). The annual

average concentration for nonanal exhibits a similar but less pronounced behavior, whereas oleic acid shows a more or less reversed spatial pattern, with highest concentrations in the western part of the air basin. It is speculated that nonanal and nonanedioic acid found in fine airborne particulate matter may be supplemented by atmospheric chemical reactions involving both oleic and palmitoleic acid. In comparing the findings for aromatic polycarboxylic acids with aliphatic dicarboxylic acids, the annual concentration distributions show similar trends with high summer and low winter concentrations.

Diterpenoid acids and their pyrolysis product retene (wood smoke markers) were found at elevated concentrations only during the heating season. This pattern closely resembles the use of wood for space heating.

Additional oxygenated compounds, nitrogen-containing organic compounds, simple hydrocarbons (n-alkanes), polycyclic aromatic hydrocarbons, and polycyclic aromatic ketones and quinones were quantified, as shown in Table 5.13.1. The highest total n-alkane concentrations were measured at Downtown Los Angeles followed by West Los Angeles, and Pasadena, reaching peak monthly average total n-alkanes values of 146 ng m^{-3} during winter 1982. All n-alkanes except n-heneitriacontane (C_{31}) show high winter and low summer concentrations. n-Heneitriacontane concentrations are elevated in spring and summer. The highest single n-alkane concentrations were found for n-pentacosane (n-C_{25}) and n-heneitriacontane (n-C_{31}). While lower n-alkane ambient concentrations ($\leq$ n-C_{26}) probably are dominated by the exhaust from vehicles fueled by gasoline and diesel oils, the higher n-alkanes ($\geq$ n-C_{29}) can be contributed from biogenic input of epicuticular plant waxes. The n-C_{29} and n-C_{31} are the dominant n-alkanes in plant waxes and their elevated atmospheric inputs in spring and summer reflect an increased biogenic input to the atmosphere at that time of the year.

Polycyclic aromatic hydrocarbons (including possibly mutagenic compounds such as benzo[a]pyrene and cyclopenta[cd]pyrene) show high winter and low summer concentrations, consistent with their origin from primary combustion processes that receive less dilution in winter than in summer. On the contrary, polycyclic aromatic ketones and quinones when compared to elemental carbon concentrations

show increased input/formation during early summer, suggesting possible atmospheric reactions involving the oxygenation of polycyclic aromatic hydrocarbons.

Table 5.13.1 Annual Average Ambient Concentrations for Fine Particle Organic Compounds found at West Los Angeles, Downtown Los Angeles, Pasadena, Riverside, and San Nicolas Island for the entire Year 1982.

Part A Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dec.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
n-Alkanes						
n-Tricosane	3.2	6.7	5.4	4.5	0.09	a
n-Tetracosane	5.0	6.4	4.7	3.9	0.23	a
n-Pentacosane	8.4	11.2	9.5	6.7	0.25	a
n-Hexacosane	7.0	8.2	4.3	5.4	0.15	a
n-Heptacosane	5.2	6.7	5.6	5.6	0.06	a
n-Octacosane	2.5	3.1	2.5	2.1	0.18	a
n-Nonacosane	6.8	7.1	4.7	5.2	0.26	a
n-Triacontane	2.4	2.7	2.5	2.5	0.22	a
n-Heneitriacontane	9.3	12.6	9.6	11.4	0.10	a
n-Dotriacontane	1.5	1.5	1.5	1.0	< 0.03	a
n-Tritriacontane	2.2	2.1	2.3	1.5	< 0.03	a
n-Tetratriacontane	0.59	0.58	0.68	0.36	< 0.03	a
n-Alkanes (C23 - C34)	54.09	68.88	53.28	50.16		
n-Alkanoic Acids						
n-Nonanoic Acid	3.3	6.6	5.3	9.9	0.24	a
n-Decanoic Acid	1.3	2.0	2.4	3.1	< 0.02	a
n-Undecanoic Acid	3.8	2.8	6.0	2.8	0.18	a
n-Dodecanoic Acid	3.7	5.3	7.0	6.3	0.19	a
n-Tridecanoic Acid	3.3	4.3	4.9	3.9	0.13	a
n-Tetradecanoic Acid	14.4	19.7	22.2	22.8	2.73	a
n-Pentadecanoic Acid	4.3	5.3	6.1	5.1	0.67	a
n-Hexadecanoic Acid	118.3	140.5	127.4	128.1	14.0	a
n-Heptadecanoic Acid	3.4	4.7	5.2	4.0	0.34	a
n-Octadecanoic Acid	57.7	59.2	50.0	41.1	2.46	a
n-Nonadecanoic Acid	0.79	1.1	1.1	0.95	0.07	a

Table 5.13.1 (continued)

Part B

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dez.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
n-Eicosanoic Acid	4.3	5.1	6.1	3.1	0.20	a
n-Heneicosanoic Acid	1.7	2.1	2.3	1.4	0.08	a
n-Docosanoic Acid	7.5	8.7	9.9	5.7	0.39	a
n-Tricosanoic Acid	2.0	2.0	2.5	1.5	0.10	a
n-Tetracosanoic Acid	12.5	11.8	16.5	9.2	0.53	a
n-Pentacosanoic Acid	1.4	1.3	1.6	1.1	0.07	a
n-Hexacosanoic Acid	7.1	5.6	9.3	5.3	0.23	a
n-Heptacosanoic Acid	0.66	0.49	0.81	0.47	0.03	a
n-Octacosanoic Acid	2.9	2.7	4.9	3.2	0.15	a
n-Nonacosanoic Acid	0.53	0.33	0.57	0.43	< 0.02	a
n-Triacontanoic Acid	1.2	1.0	2.2	2.2	< 0.02	a
n-Alkanoic Acids (C9 - C30)	256.08	292.62	294.28	261.68		
n-Alkenoic Acids						
n-Octadecenoic Acid	23.6	24.8	26.0	17.3	< 0.02	a
n-Alkanals						
Nonanal	6.9	5.7	9.5	7.5	0.67	b
Aliphatic Dicarboxylic Acids						
Propanedioic Acid (Malonic Acid)	28.0	32.7	44.4	51.0	< 0.02	a
2-Butenedioic Acid	0.58	0.66	1.3	0.84	< 0.02	a
Butanedioic Acid (Succinic Acid)	55.0	66.5	51.2	84.1	< 0.02	a
Methylbutanedioic Acid (Methylsuccinic Acid)	11.6	18.0	15.0	20.3	< 0.02	a
Pentanedioic Acid (Glutaric Acid)	28.4	32.3	28.3	38.7	< 0.02	a
Methylpentanedioic Acid (Methylglutaric Acid)	15.5	19.3	16.6	23.7	< 0.02	a
Hydroxybutanedioic Acid (Hydroxysuccinic Acid)	7.8	14.3	16.0	22.1	< 0.02	a
Hexanedioic Acid (Adipic Acid)	15.0	14.1	14.1	24.3	< 0.02	a
Octanedioic Acid	2.9	3.4	4.1	2.5	< 0.02	a
Nonanedioic Acid (Azelaic Acid)	34.2	29.0	22.8	44.7	< 0.02	a
Aliphatic Dicarboxylic Acids (C_3 - C_9)	198.98	230.26	213.8	312.24		

Table 5.13.1 (continued)

Part C

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dez.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
Diterpenoid Acids and Retene[c]						
Dehydroabietic Acid	20.9	23.6	22.6	10.2	< 0.03	a
13-Isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic Acid	0.75	0.63	1.2	0.30	< 0.03	b
8,15-Pimaradien-18-oic Acid	1.1	0.44	0.57	0.07	< 0.03	b
Pimaric Acid	3.0	2.3	4.8	0.94	< 0.03	a
Isopimaric Acid	1.2	1.3	2.3	0.71	< 0.03	b
7-Oxodehydroabietic Acid	3.5	3.4	4.1	1.9	< 0.03	a
Sandaracopimaric Acid	1.4	1.6	2.2	0.60	< 0.03	b
Retene	0.10	0.07	0.06	0.01	< 0.01	a
Wood Smoke Markers	31.95	33.34	37.63	14.73		
Aromatic Polycarboxylic Acids						
1,2-Benzenedicarboxylic Acid	60.6	60.0	55.7	53.5	< 0.03	a
1,3-Benzenedicarboxylic Acid	2.1	3.4	2.9	2.1	< 0.03	a
1,4-Benzenedicarboxylic Acid	1.3	2.8	1.5	0.88	< 0.03	a
1,2,4-Benzenetricarboxylic Acid	0.45	0.52	0.84	0.67	< 0.03	a
1,3,5-Benzenetricarboxylic Acid	11.3	20.6	17.2	22.6	< 0.03	a
4-Methyl-1,2-benzenedicarboxylic Acid	15.2	27.8	28.8	26.3	< 0.03	a
1,2,4,5-Benzenetetracarboxylic Acid	0.67	0.74	0.80	0.40	< 0.03	a
Aromatic Polycarboxylic Acids	91.72	115.86	107.74	106.45		
Polycyclic Aromatic Hydrocarbons						
Fluoranthene	0.09	0.15	0.13	0.07	< 0.01	a
Pyrene	0.12	0.26	0.17	0.14	< 0.01	a
Benz[a]anthracene	0.19	0.29	0.25	0.09	< 0.01	a
Cyclopenta[cd]pyrene	0.20	0.23	0.41	0.04	< 0.01	b
Benzo[ghi]fluoranthene	0.19	0.39	0.30	0.11	< 0.01	b
Chrysene/Triphenylene	0.30	0.61	0.43	0.23	< 0.01	a
Benzo[k]fluoranthene	1.03	1.15	1.20	0.33	< 0.01	a
Benzo[b]fluoranthene	0.77	1.23	0.85	0.68	< 0.01	a

Table 5.13.1 (continued)

Part D

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dez.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
Benzo[e]pyrene	0.93	0.97	0.93	0.38	< 0.01	a
Benzo[a]pyrene	0.32	0.42	0.44	0.18	< 0.01	a
Indeno[1,2,3-cd]pyrene	0.43	0.37	0.42	0.07	< 0.01	b
Indeno[1,2,3-cd]fluoranthene	0.85	1.05	1.09	0.26	< 0.01	a
Benzo[ghi]perylene	4.11	4.47	4.43	1.12	< 0.01	a
Coronene	2.41	N.M[d]	N.M[d]	N.M[d]	< 0.01	a
Polycyclic Aromatic Hydrocarbons	11.92	11.59	11.04	3.70		
Polycyclic Aromatic Ketones and Quinones						
7H-Benz[de]anthracen-7-one	0.62	0.81	0.84	0.25	< 0.01	a
Benz[a]anthracene-7,12-dione	0.18	0.21	0.25	0.12	< 0.01	a
Benzo[cd]pyrenone	0.97	0.80	1.24	0.02	< 0.01	b
Polycyclic Aromatic Ketones and Quinones	1.77	1.82	2.33	0.39		
N-Containing Compounds						
3-Methoxypyridine	0.50	0.86	1.4	0.46	< 0.03	b
Isoquinoline	0.61	1.1	1.1	0.74	< 0.03	b
1-Methylisoquinoline	1.1	0.27	0.24	0.51	< 0.03	b
1,2-Dimethoxy-4-nitro-benzene	1.0	1.8	3.9	0.22	< 0.03	b
N-Containing Compounds	3.21	4.03	6.64	1.93		

[a] samples were available only for July to December 1982;

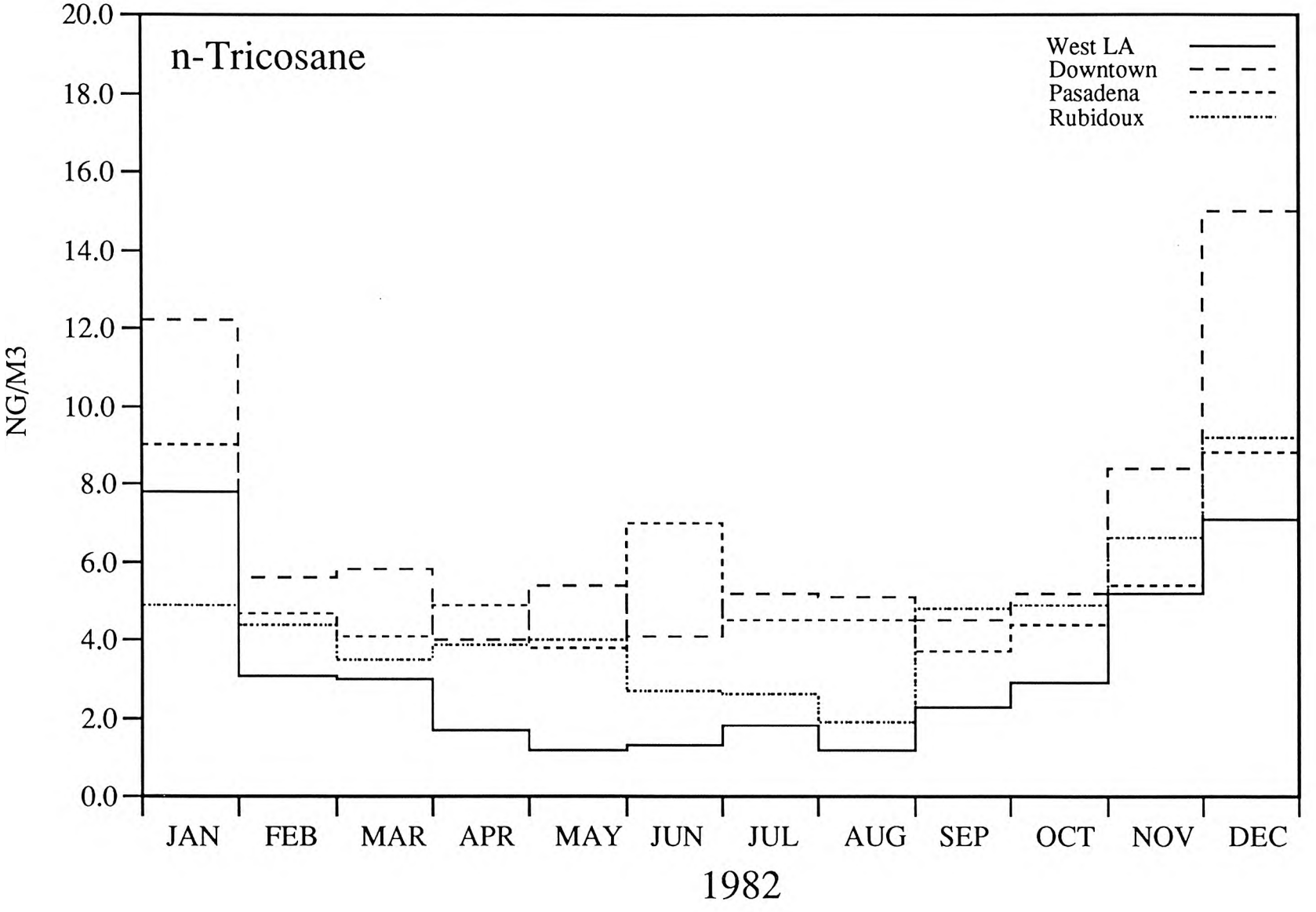
[b] for more detail see text;

[c] wood smoke markers: diterpenoid acids and retene usually were identified only during heating seasons, the annual average concentrations were calculated considering all 12 months of the year; hence, the average concentrations during heating seasons are higher;

[d] N.M. = not measured.

Appendix A1

Ambient Concentration Profiles for n-Alkanes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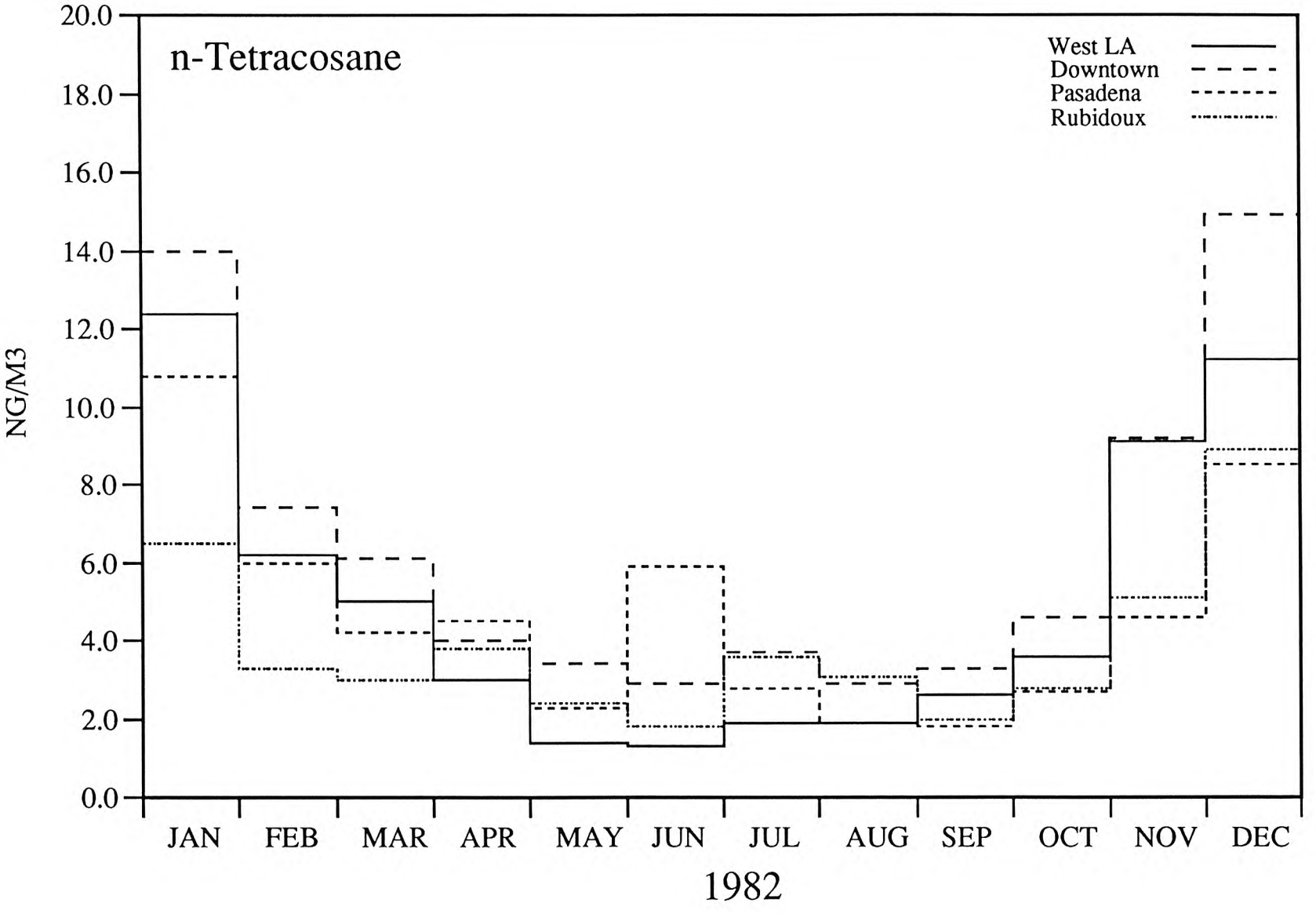
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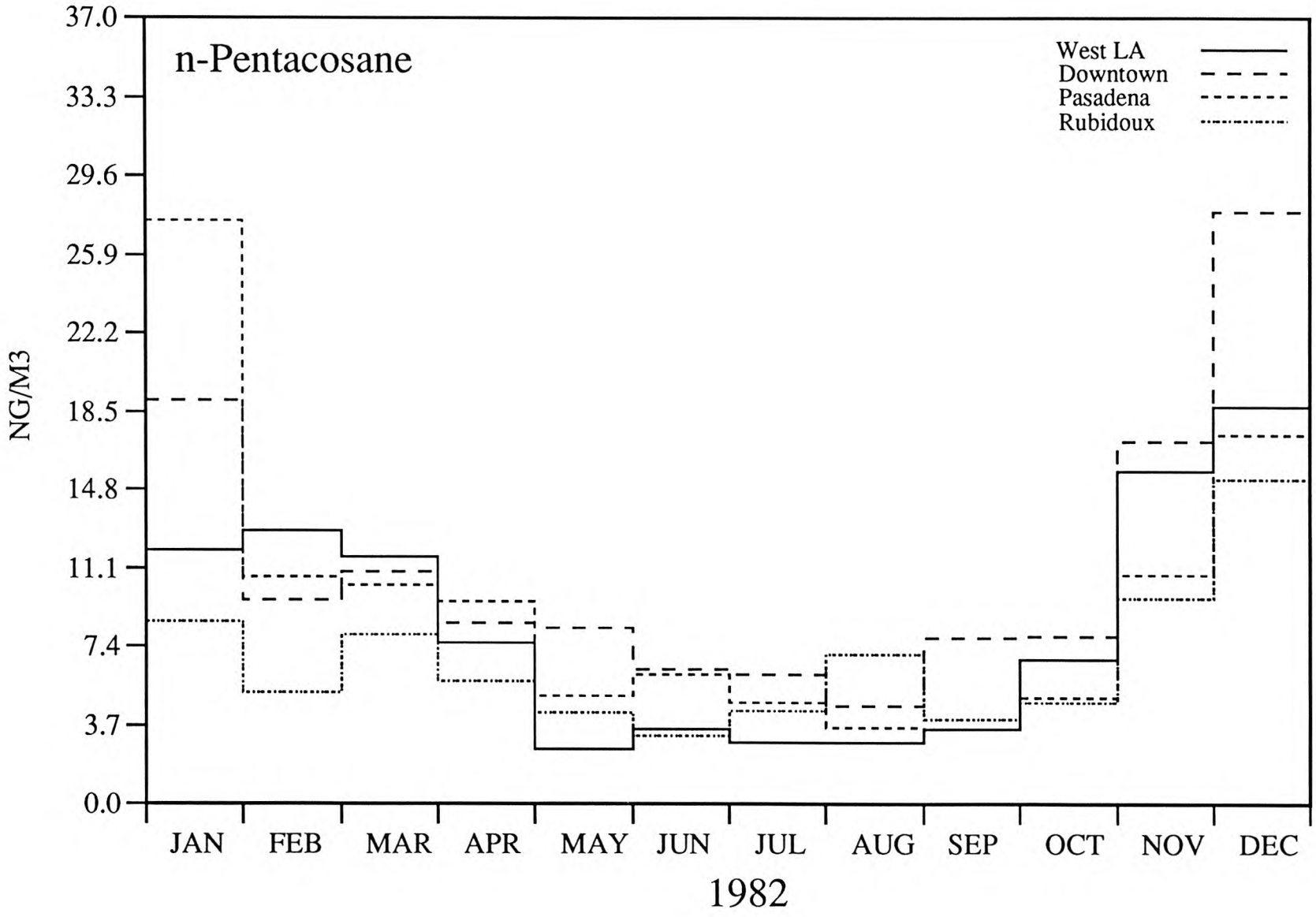
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11.1
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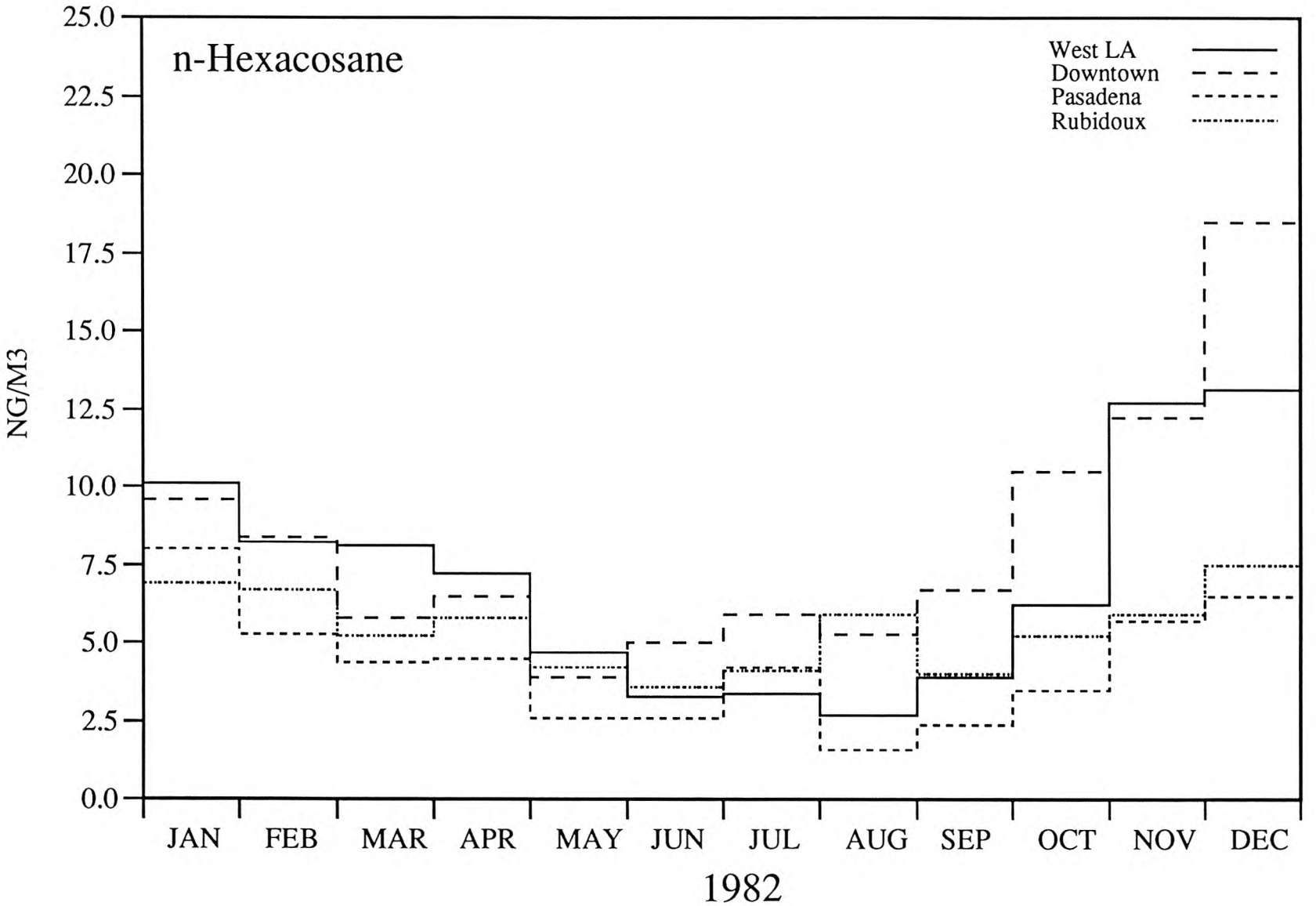
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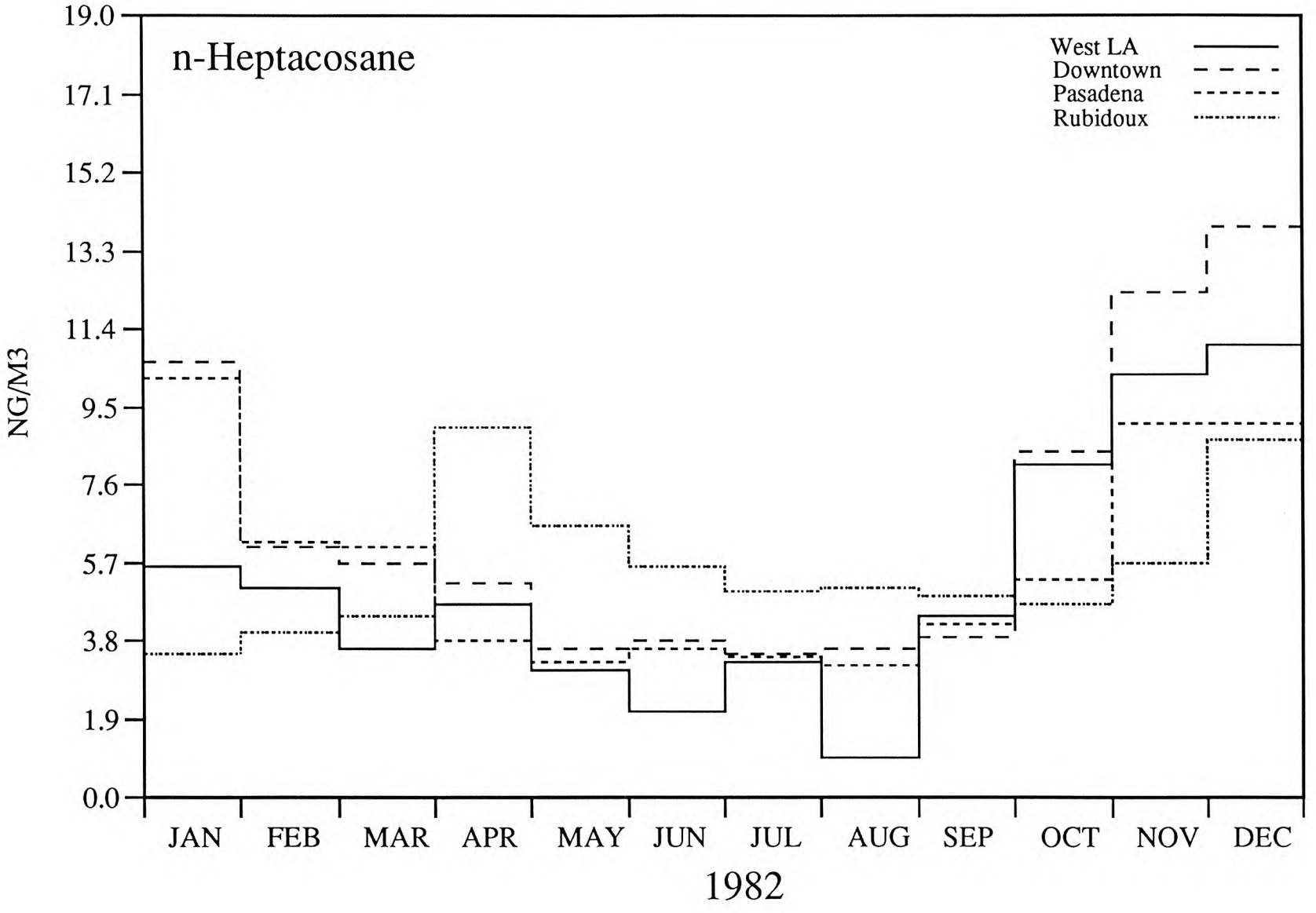
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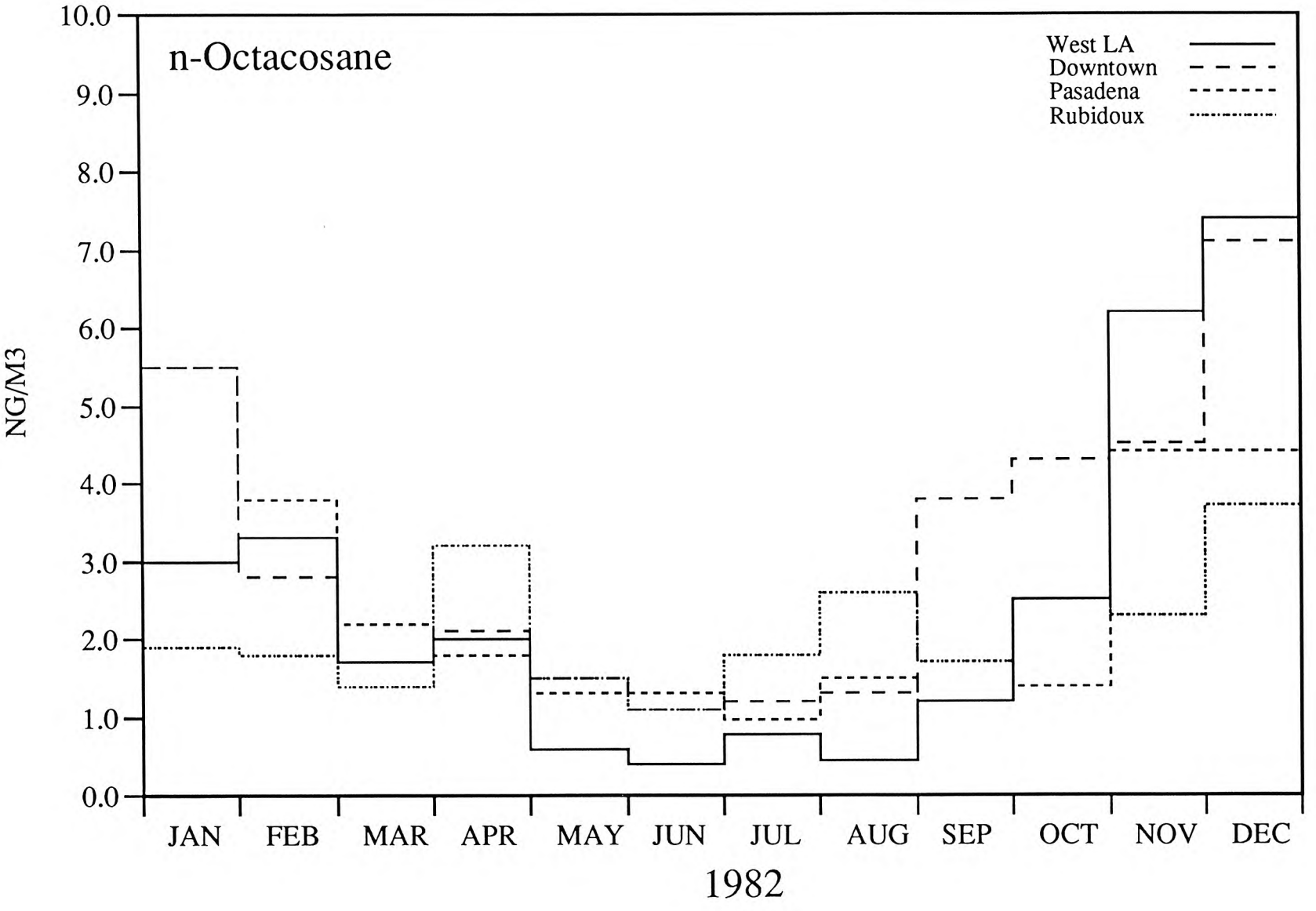
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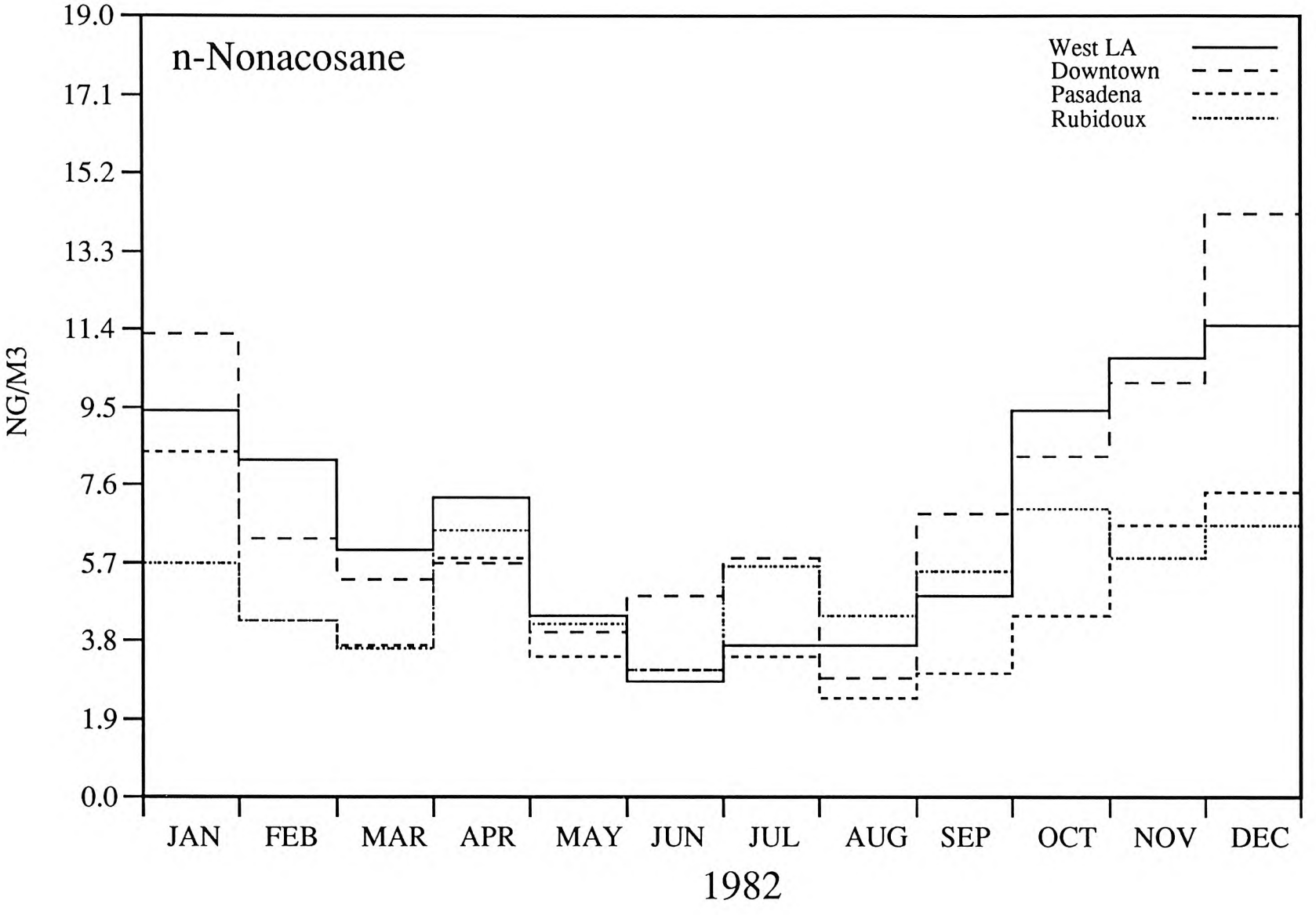
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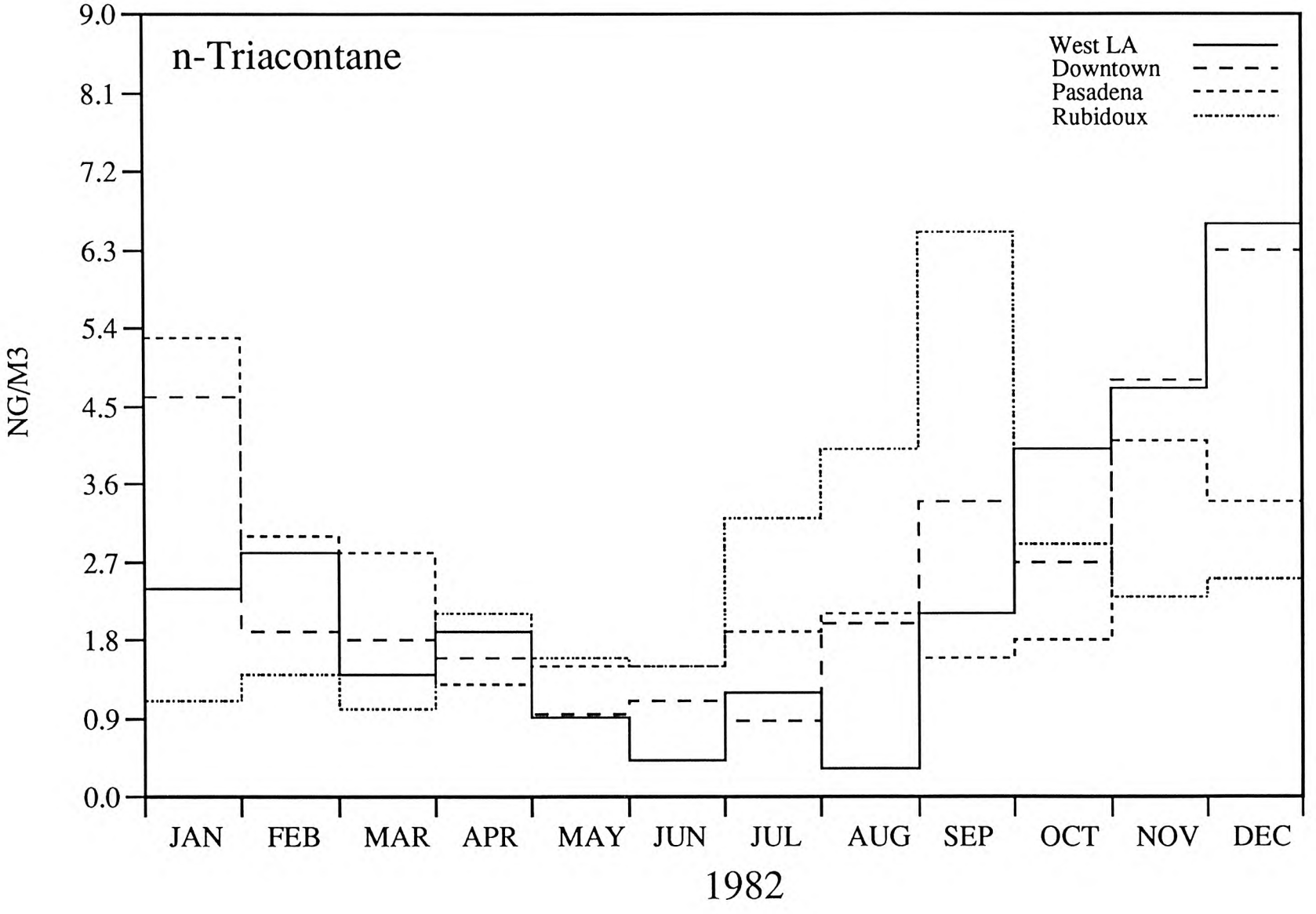
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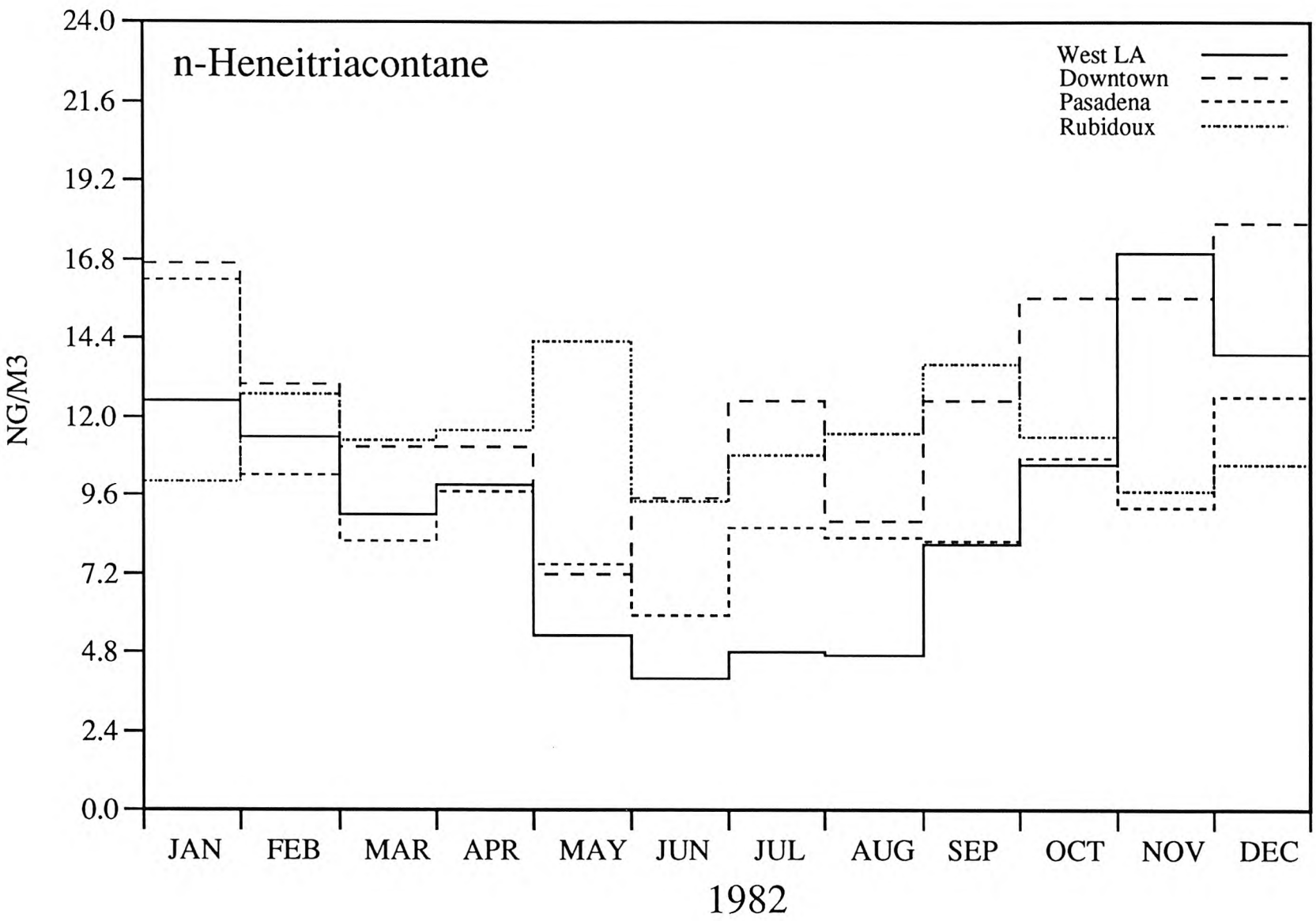
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7.2
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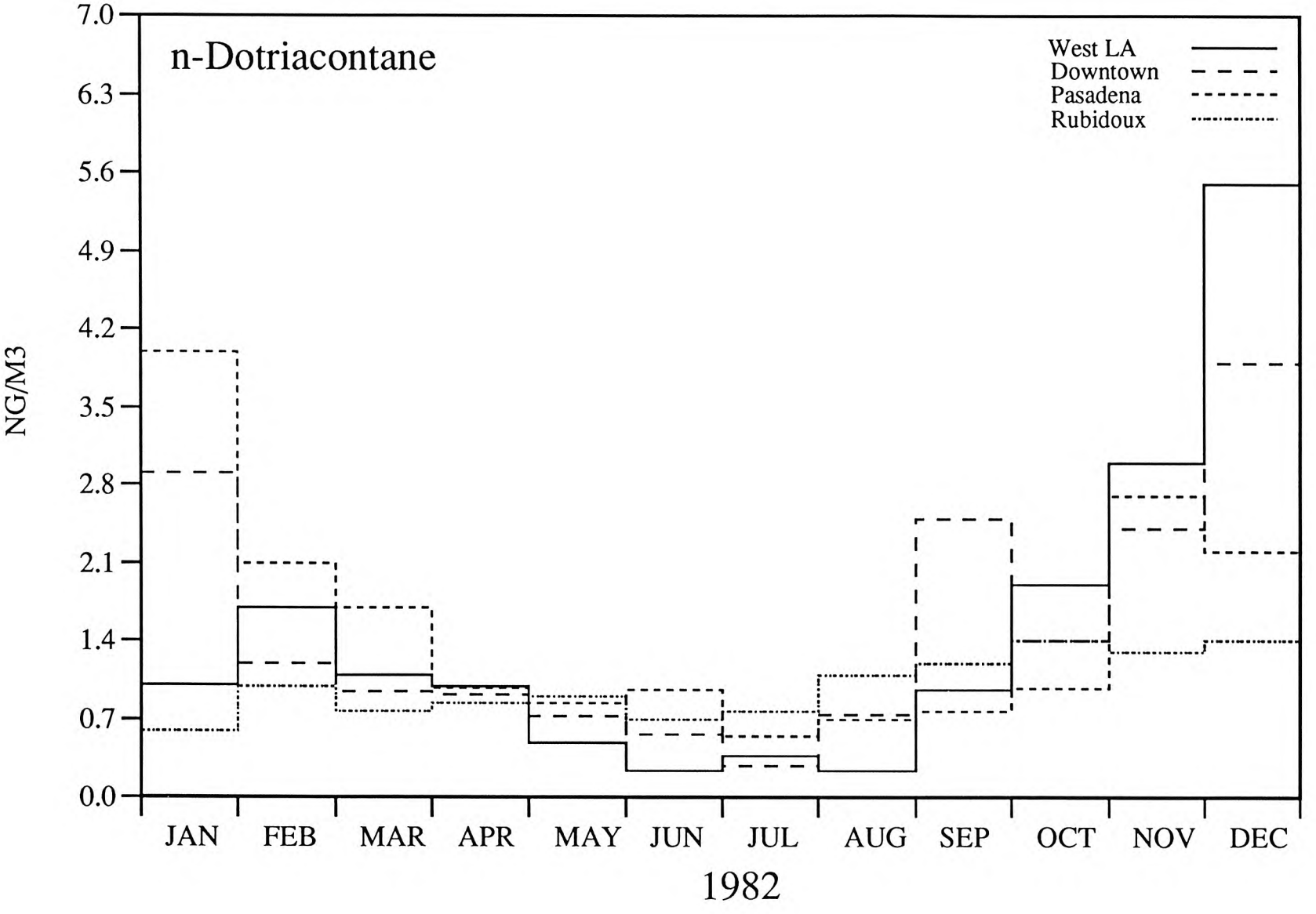
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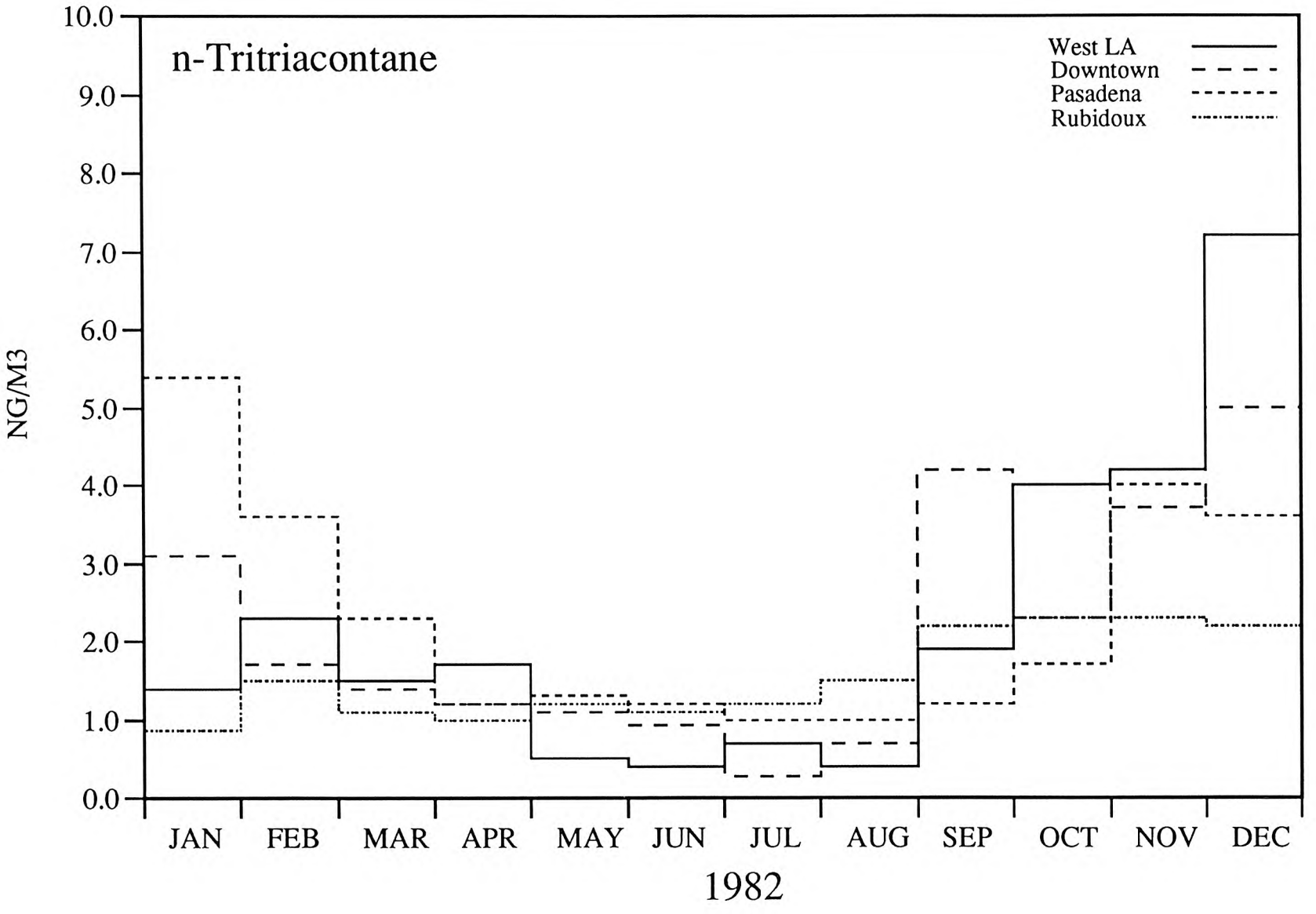
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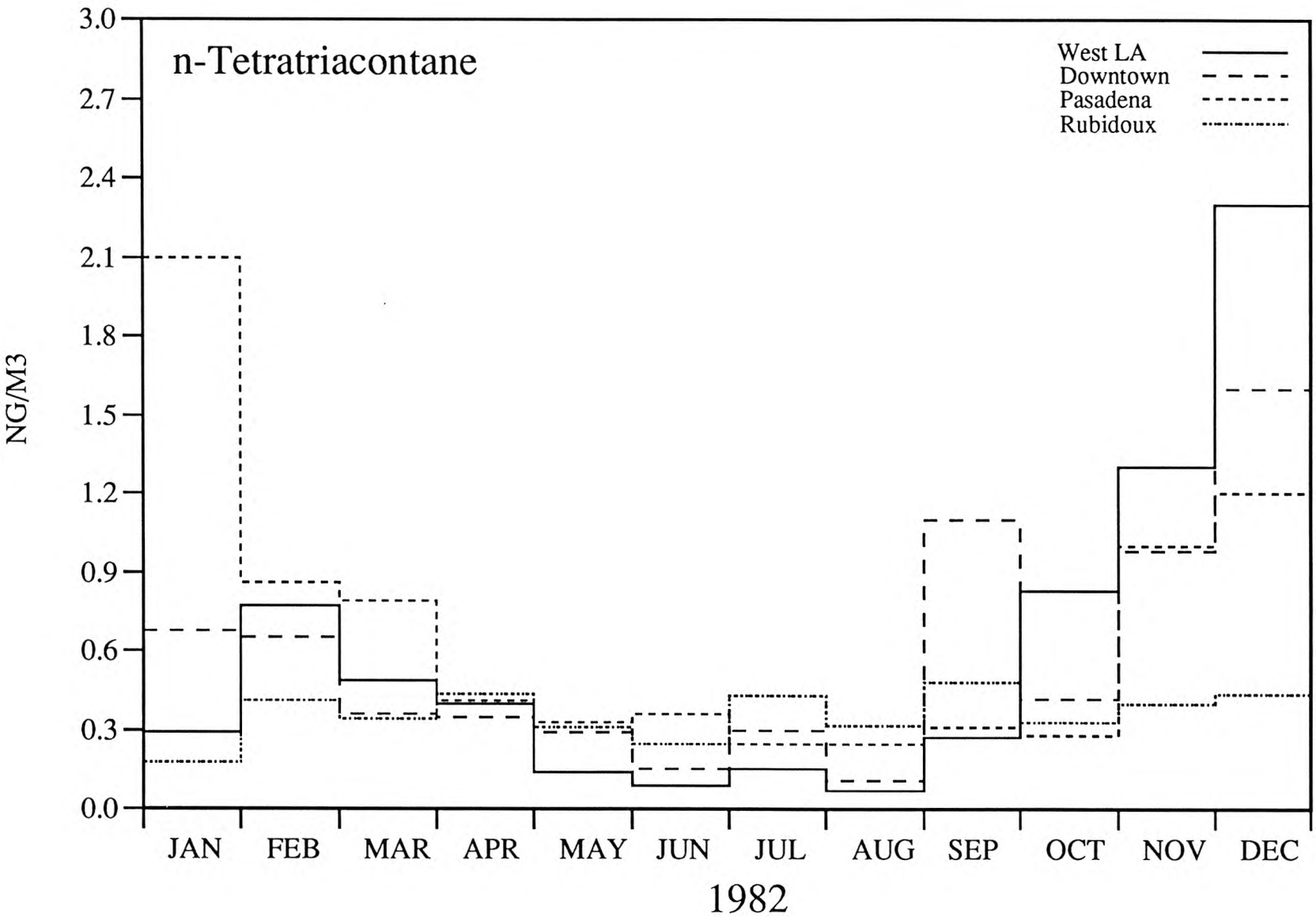
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Pasadena
Rubidoux
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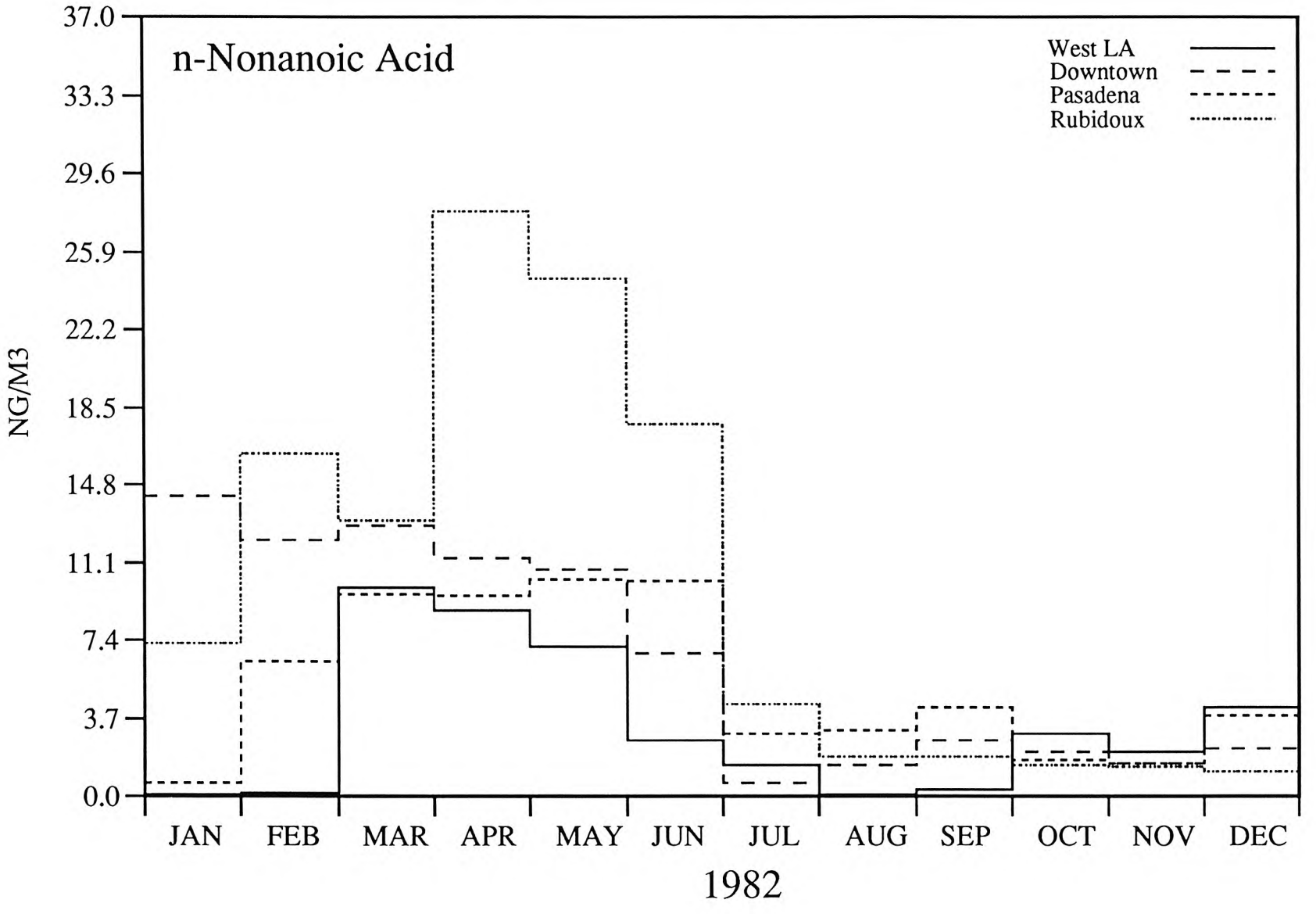
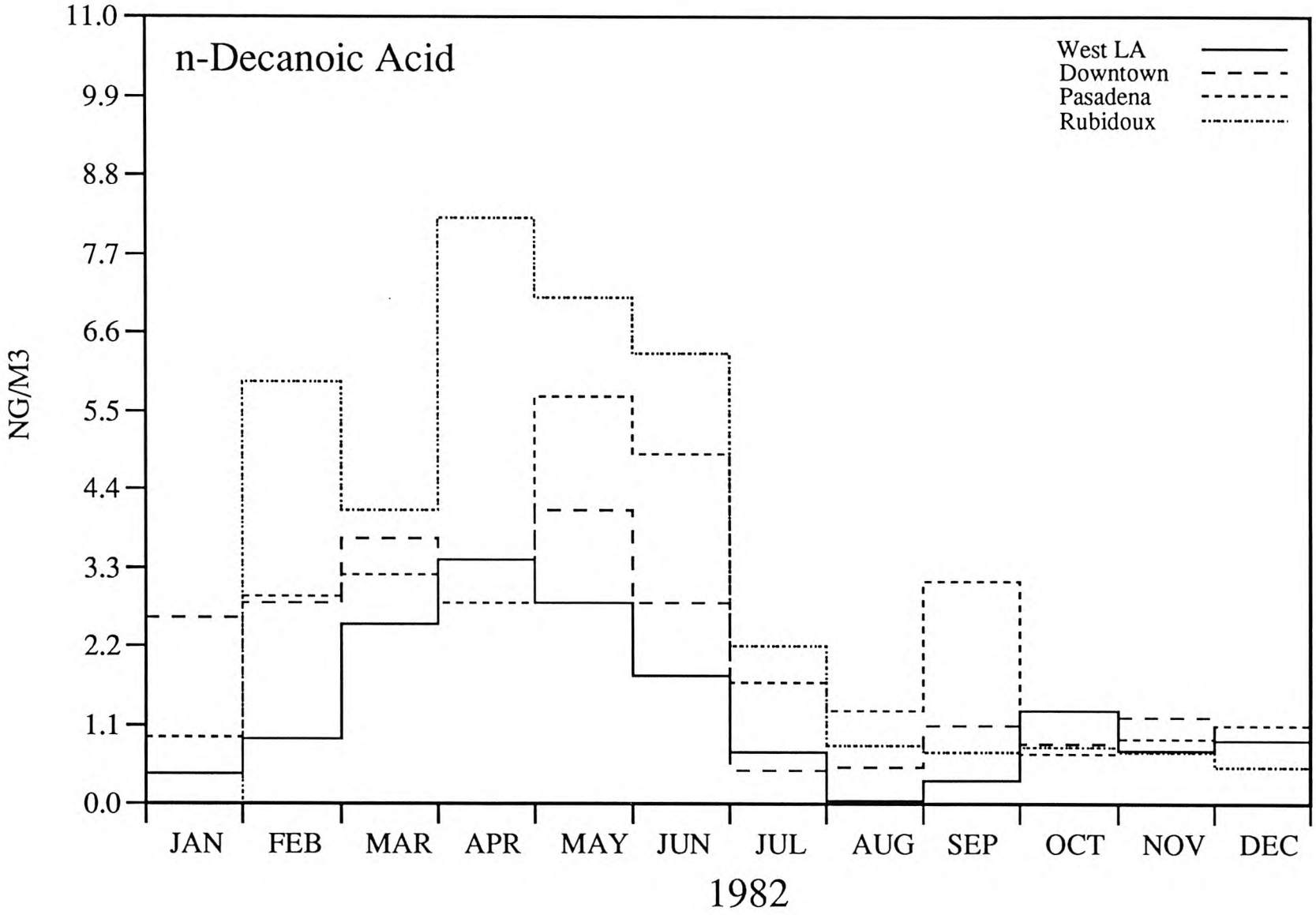
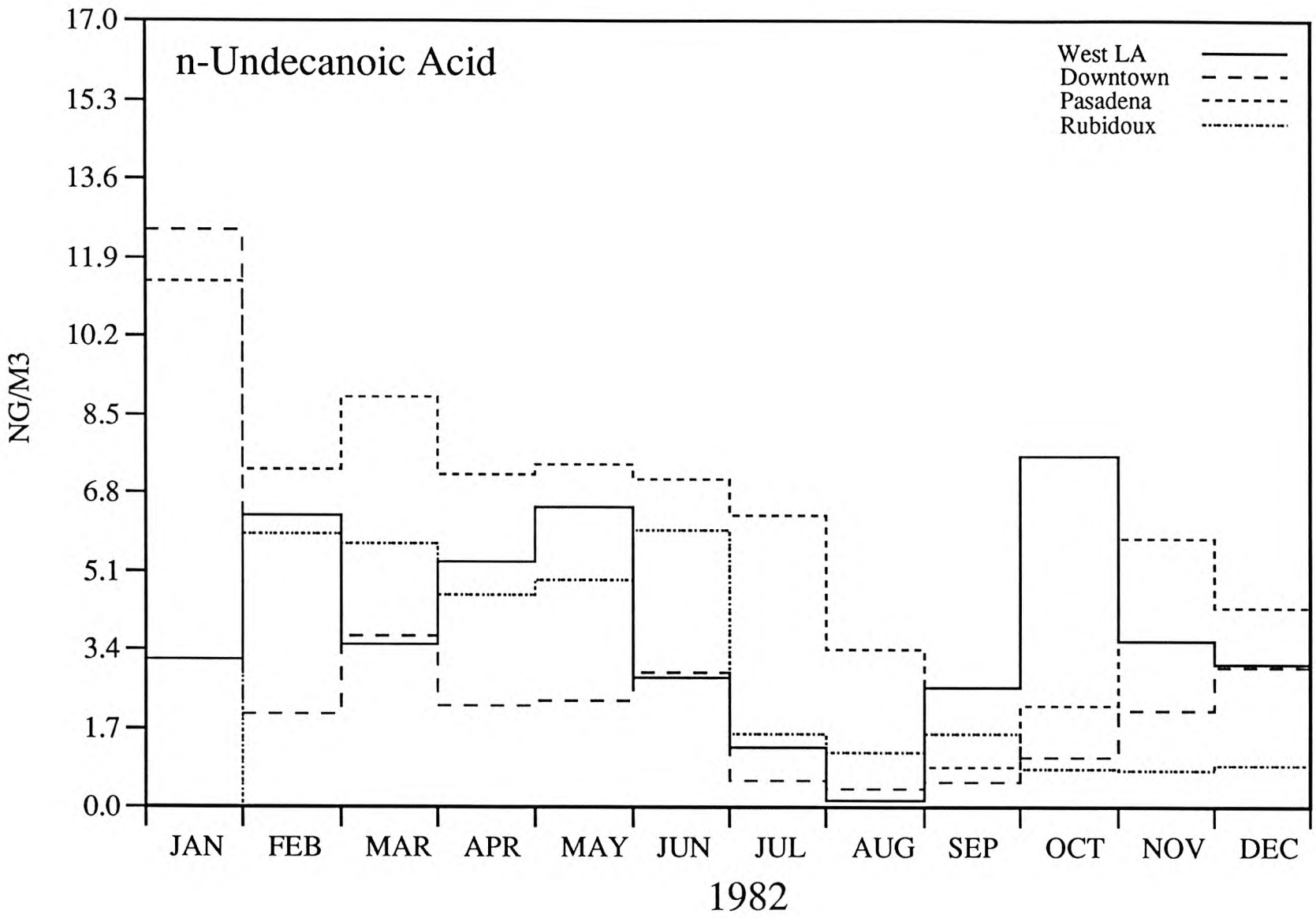
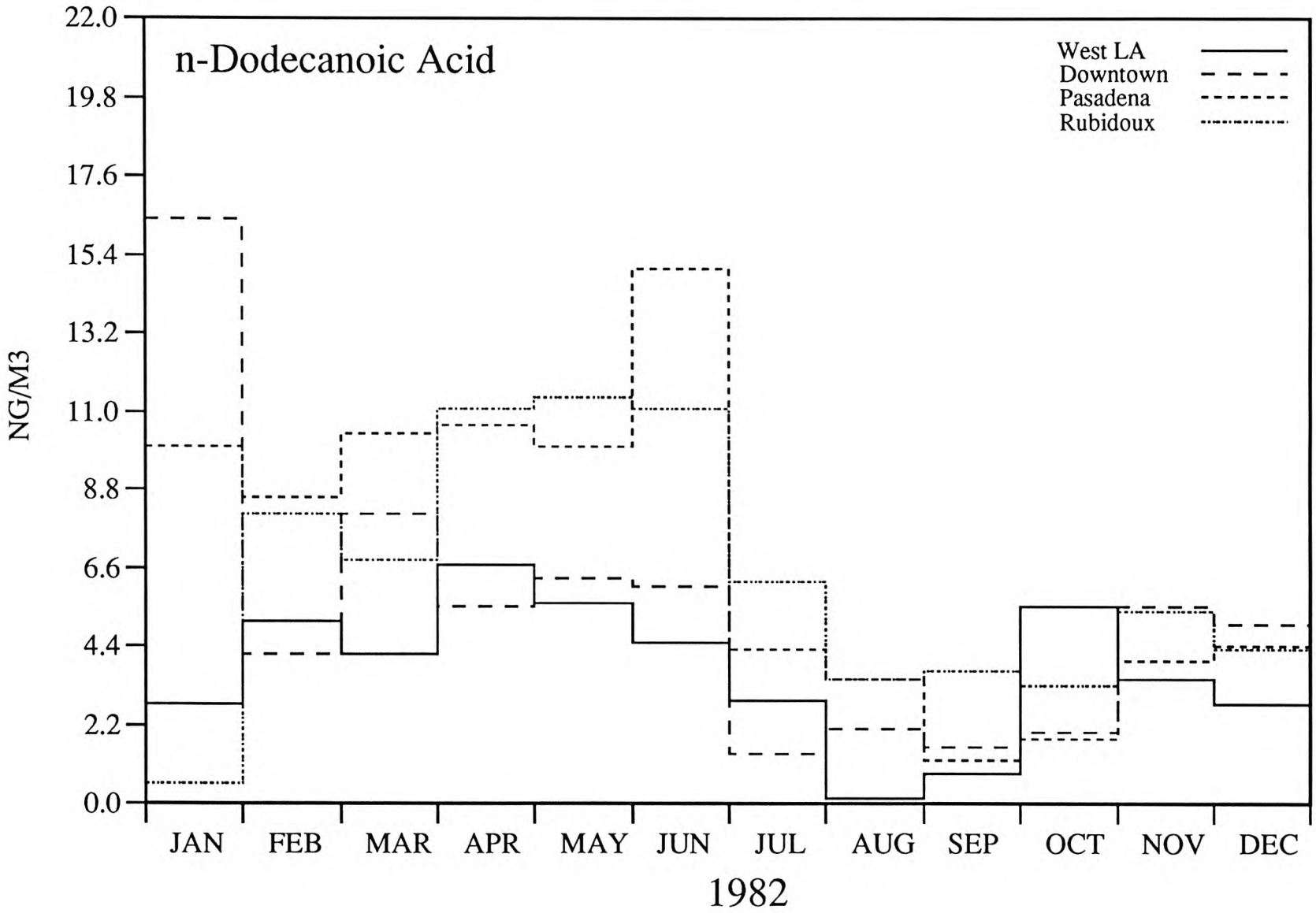
Appendix A2

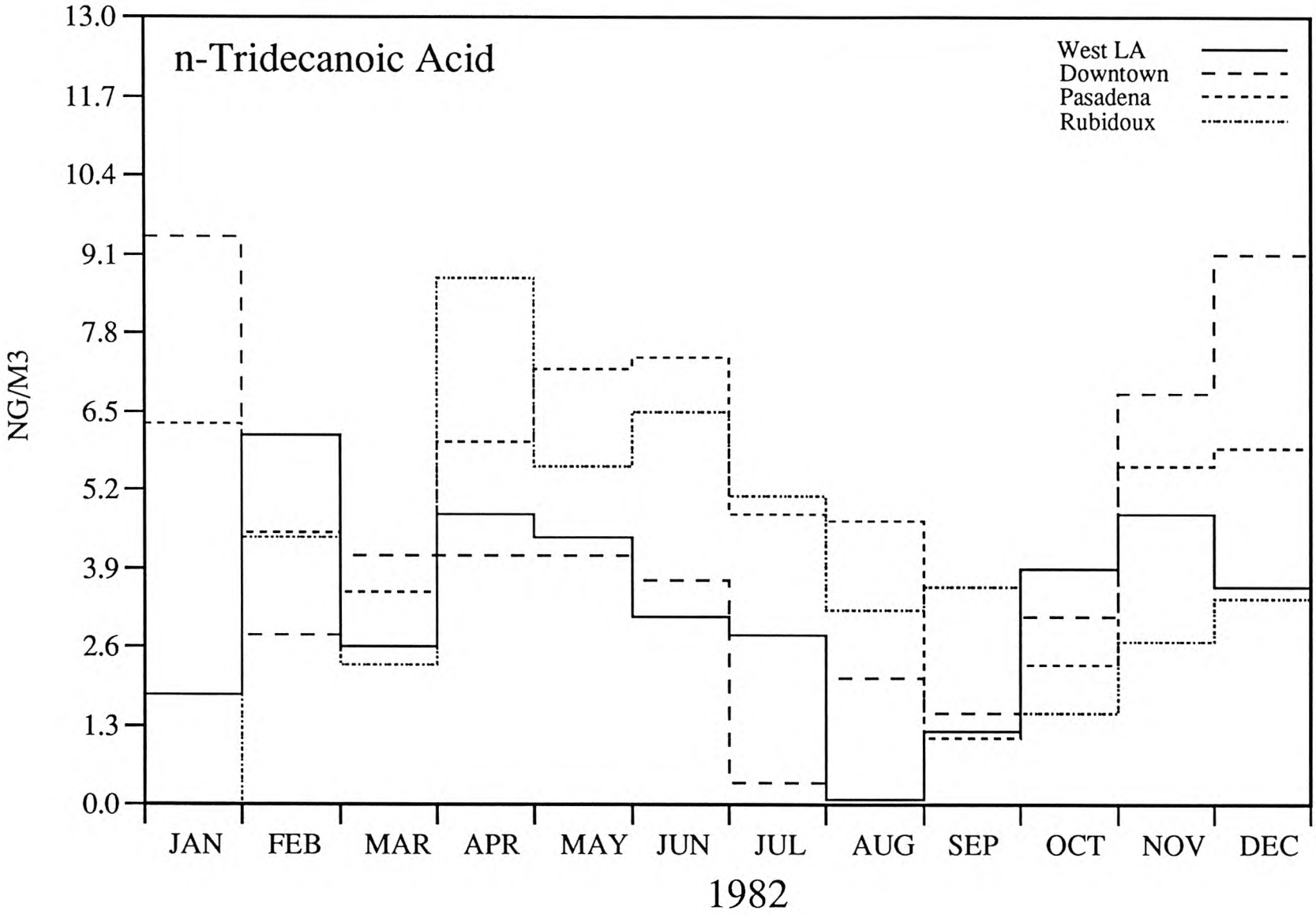
Ambient Concentration Profiles for n-Alkanoic Acids

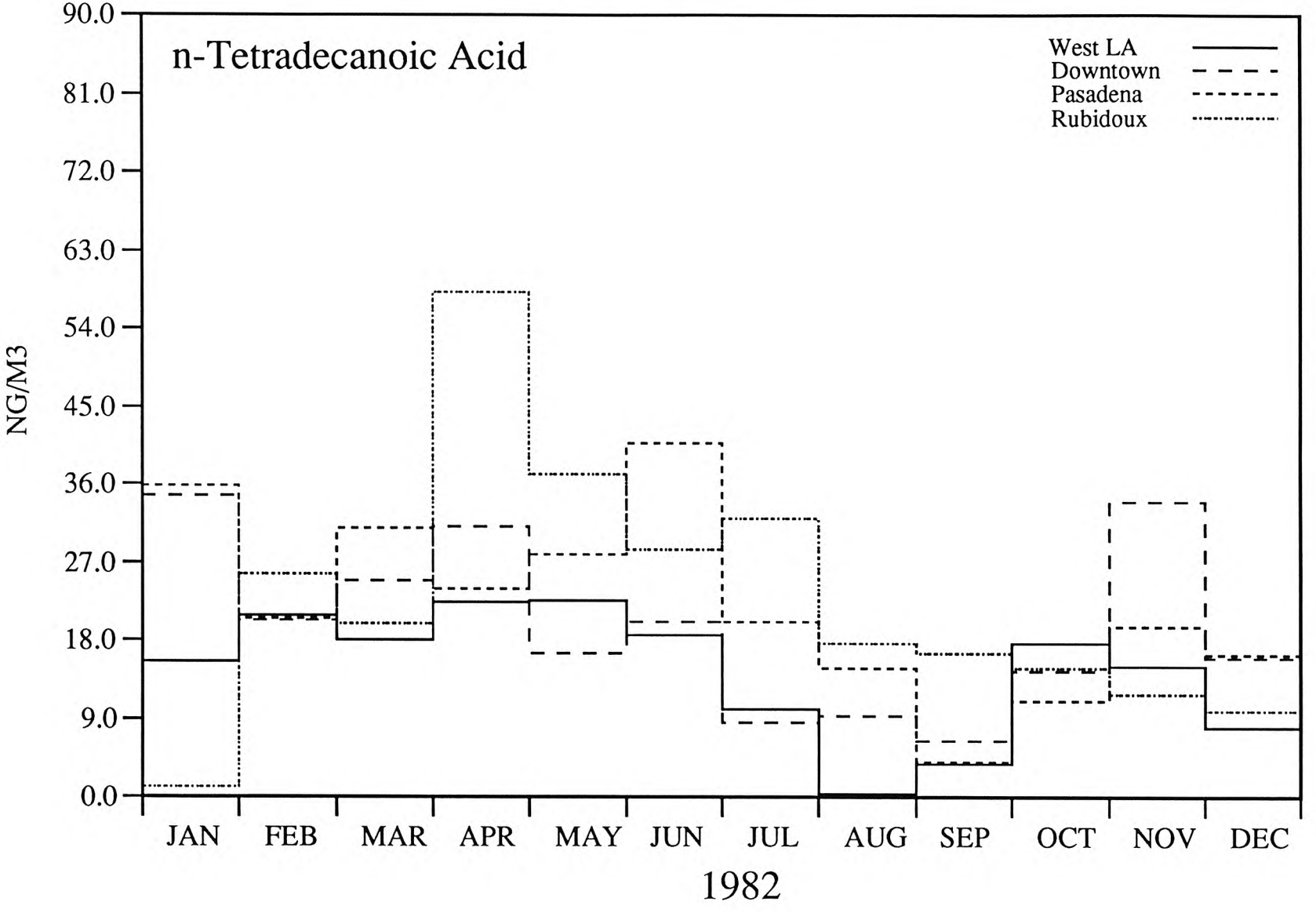

n-Nonanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
37.0
33.3
29.6
25.9
22.2
18.5
14.8
11.1
7.4
3.7
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

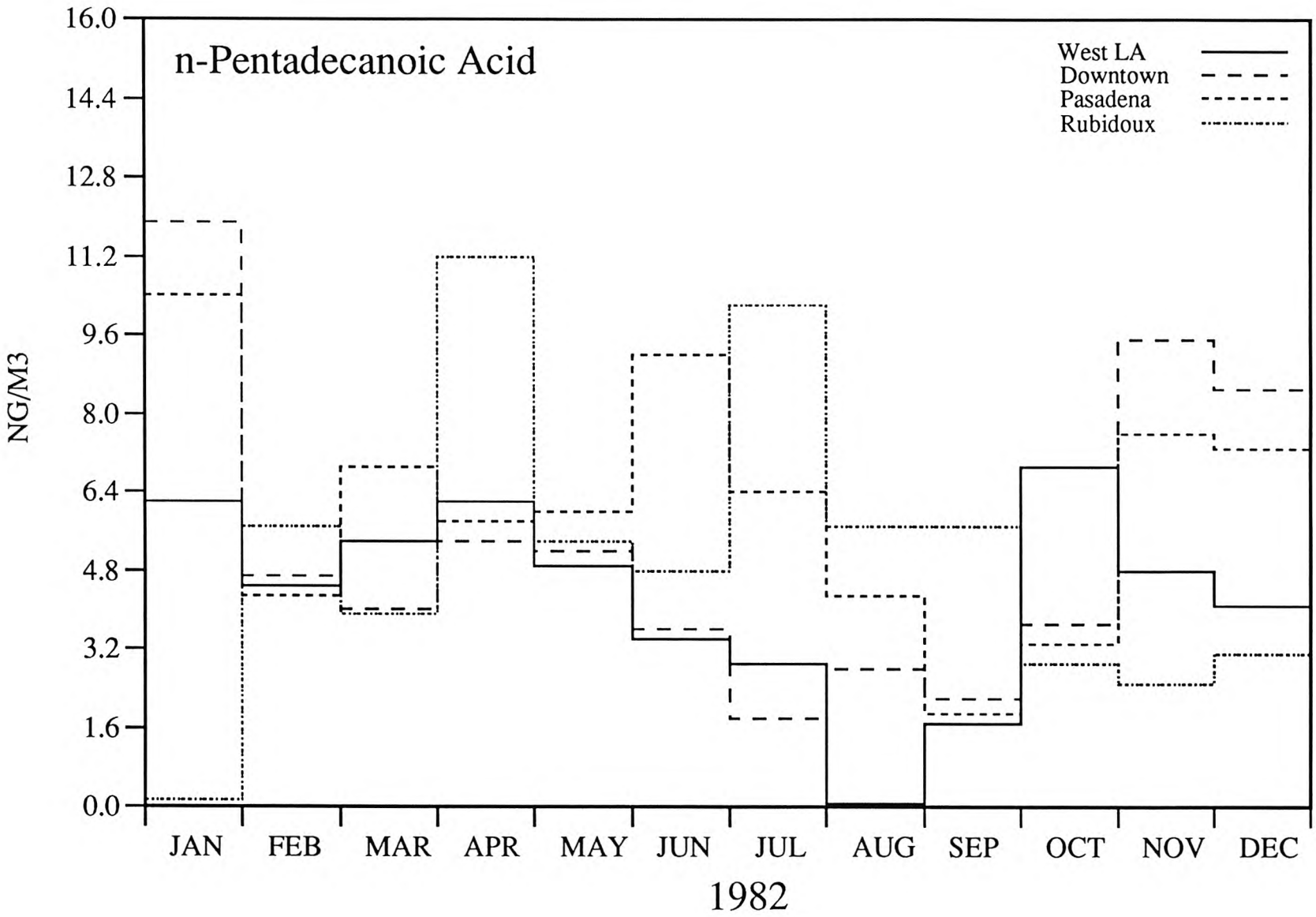

n-Decanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
11.0
9.9
8.8
7.7
6.6
5.5
4.4
3.3
2.2
1.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

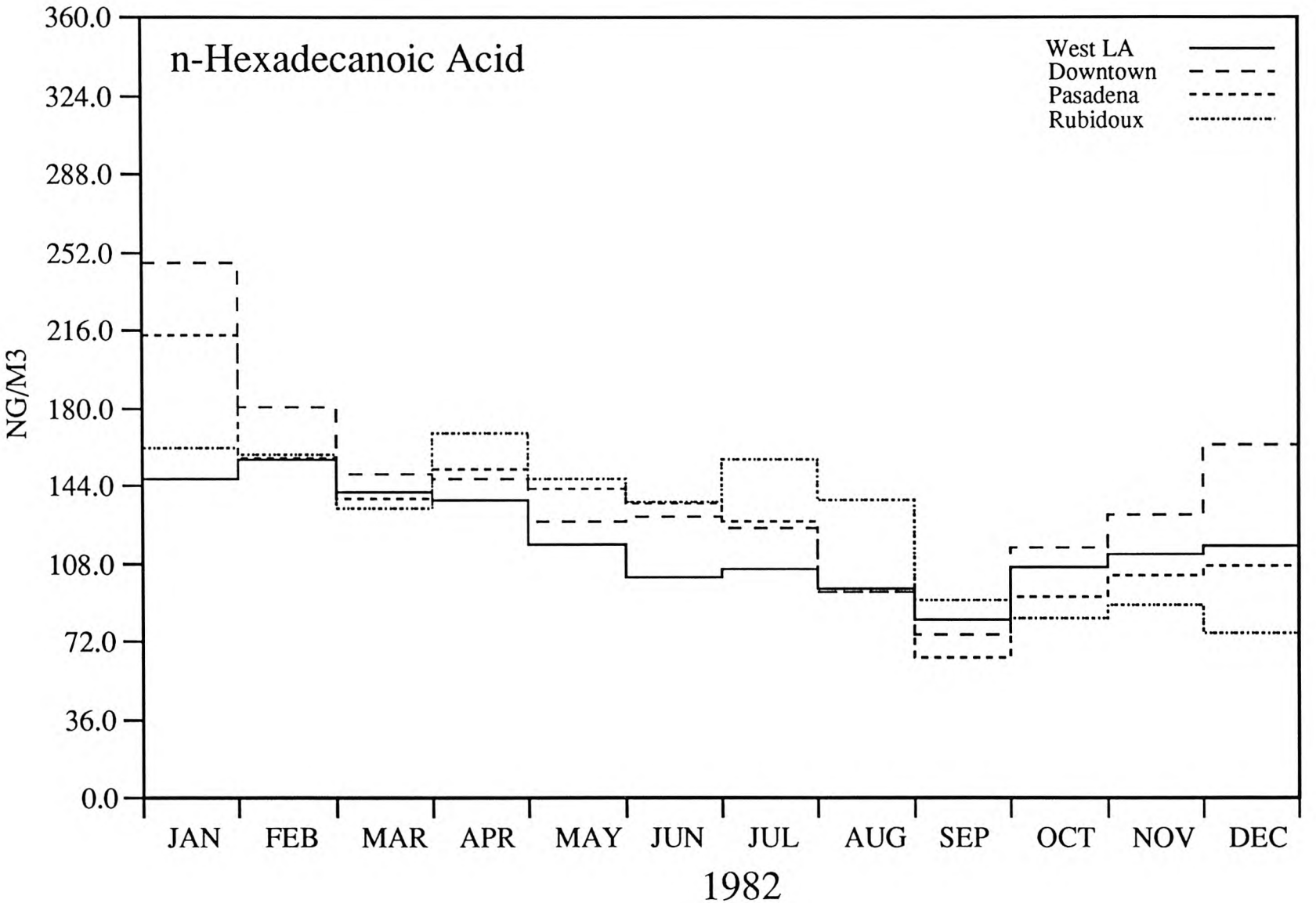

n-Undecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
17.0
15.3
13.6
11.9
10.2
8.5
6.8
5.1
3.4
1.7
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

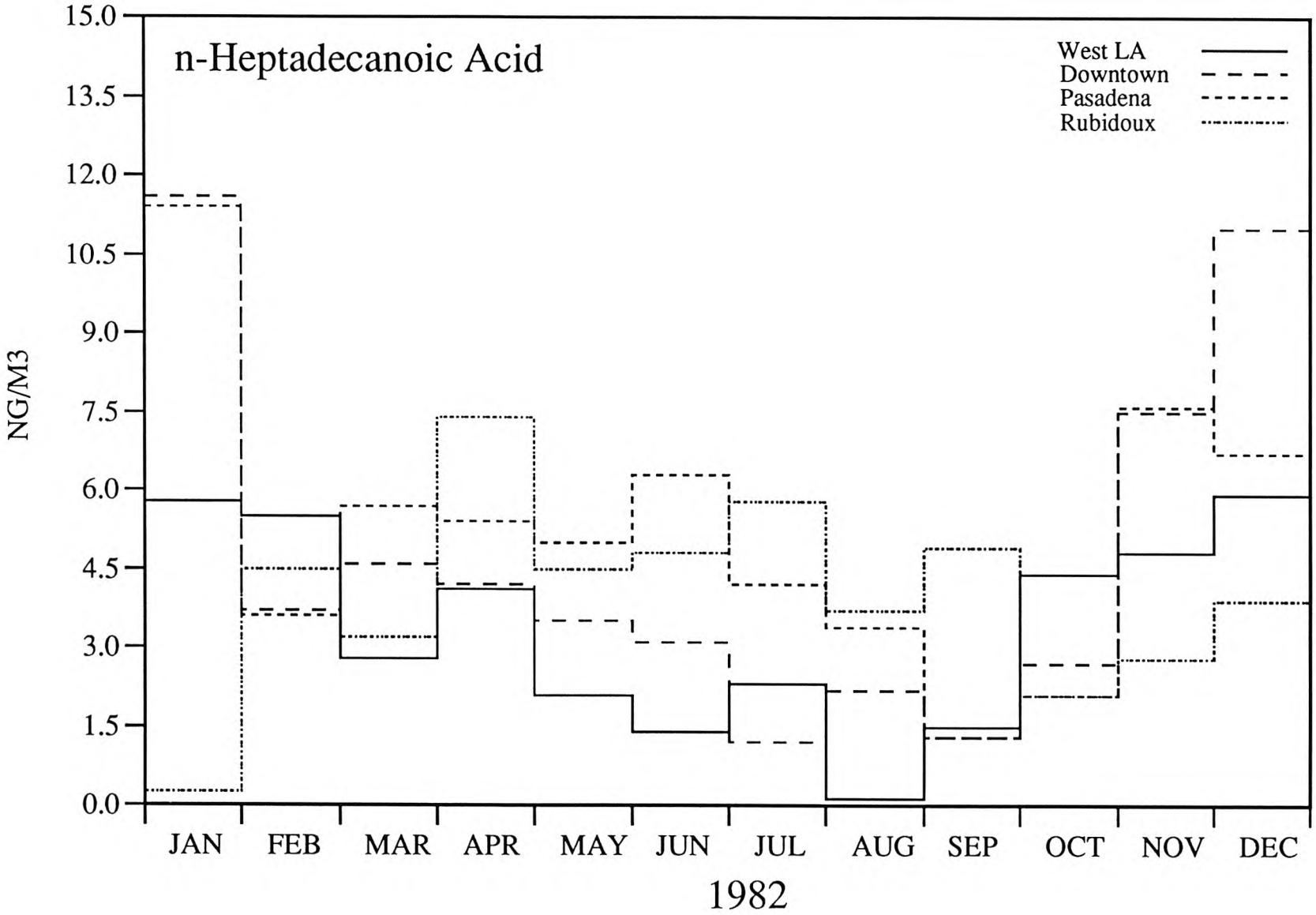

n-Dodecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
22.0
19.8
17.6
15.4
13.2
11.0
8.8
6.6
4.4
2.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

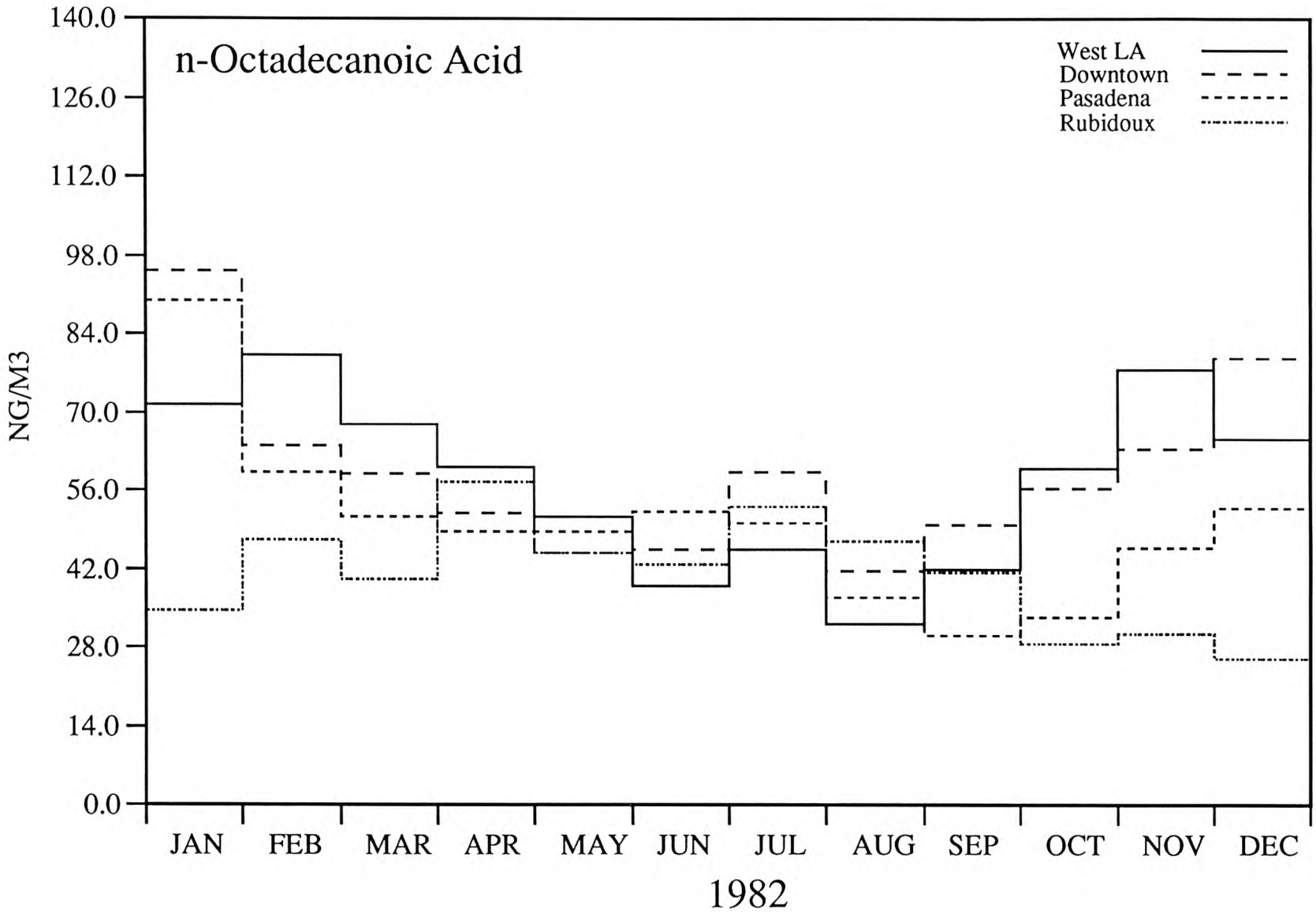

n-Tridecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
13.0
11.7
10.4
9.1
7.8
6.5
5.2
3.9
2.6
1.3
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

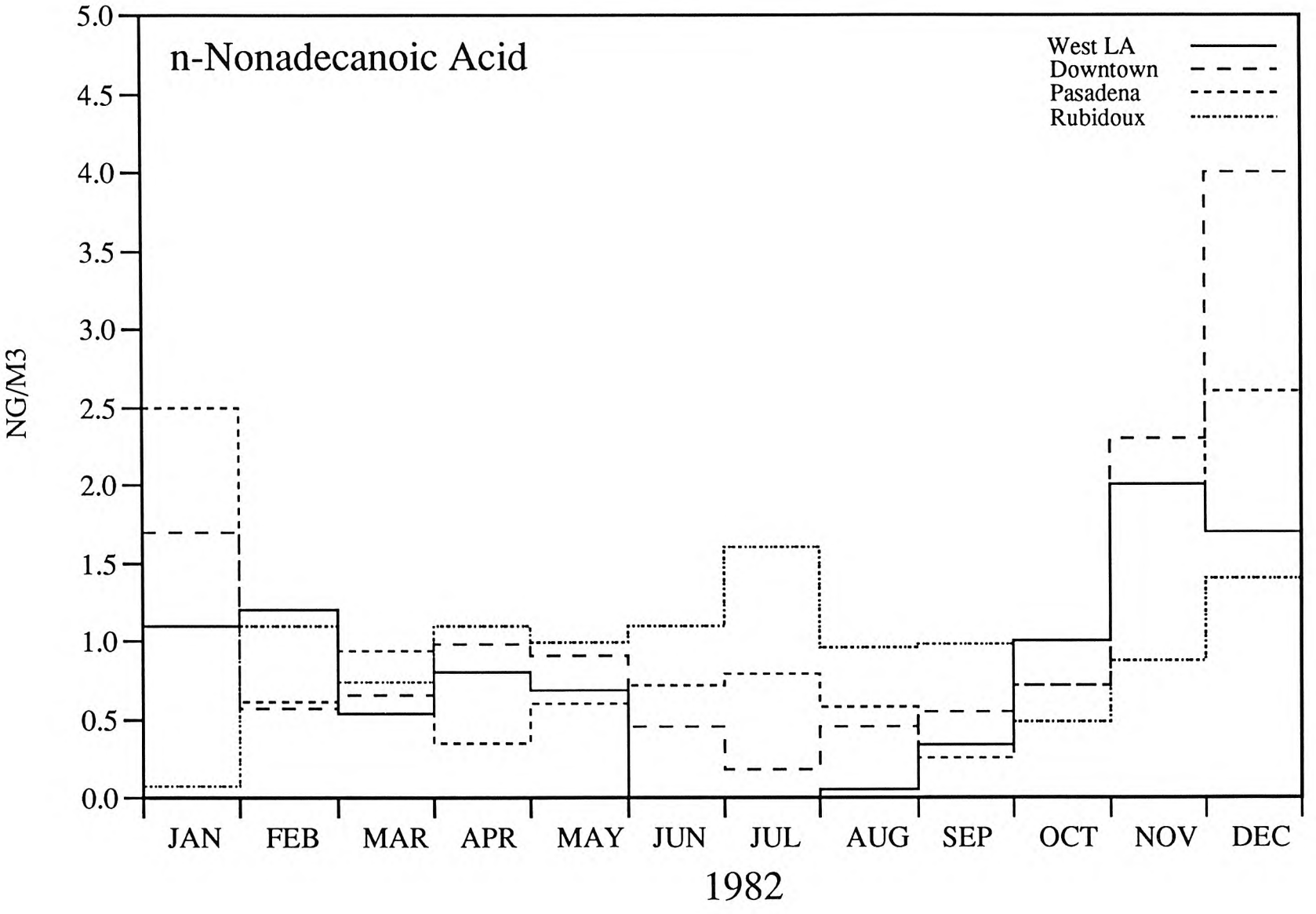

n-Tetradecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
90.0
81.0
72.0
63.0
54.0
45.0
36.0
27.0
18.0
9.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

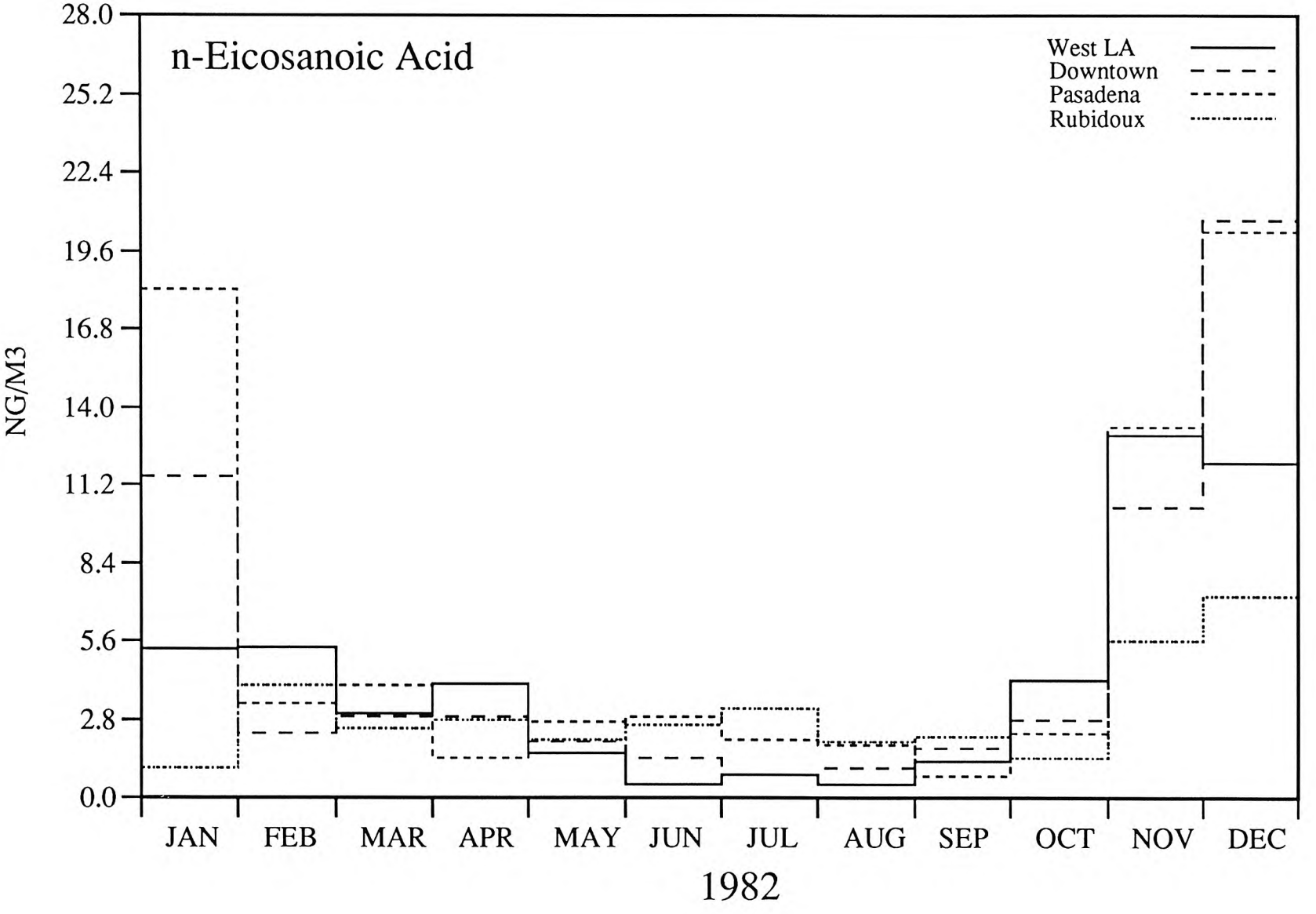

n-Pentadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
16.0
14.4
12.8
11.2
9.6
8.0
6.4
4.8
3.2
1.6
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

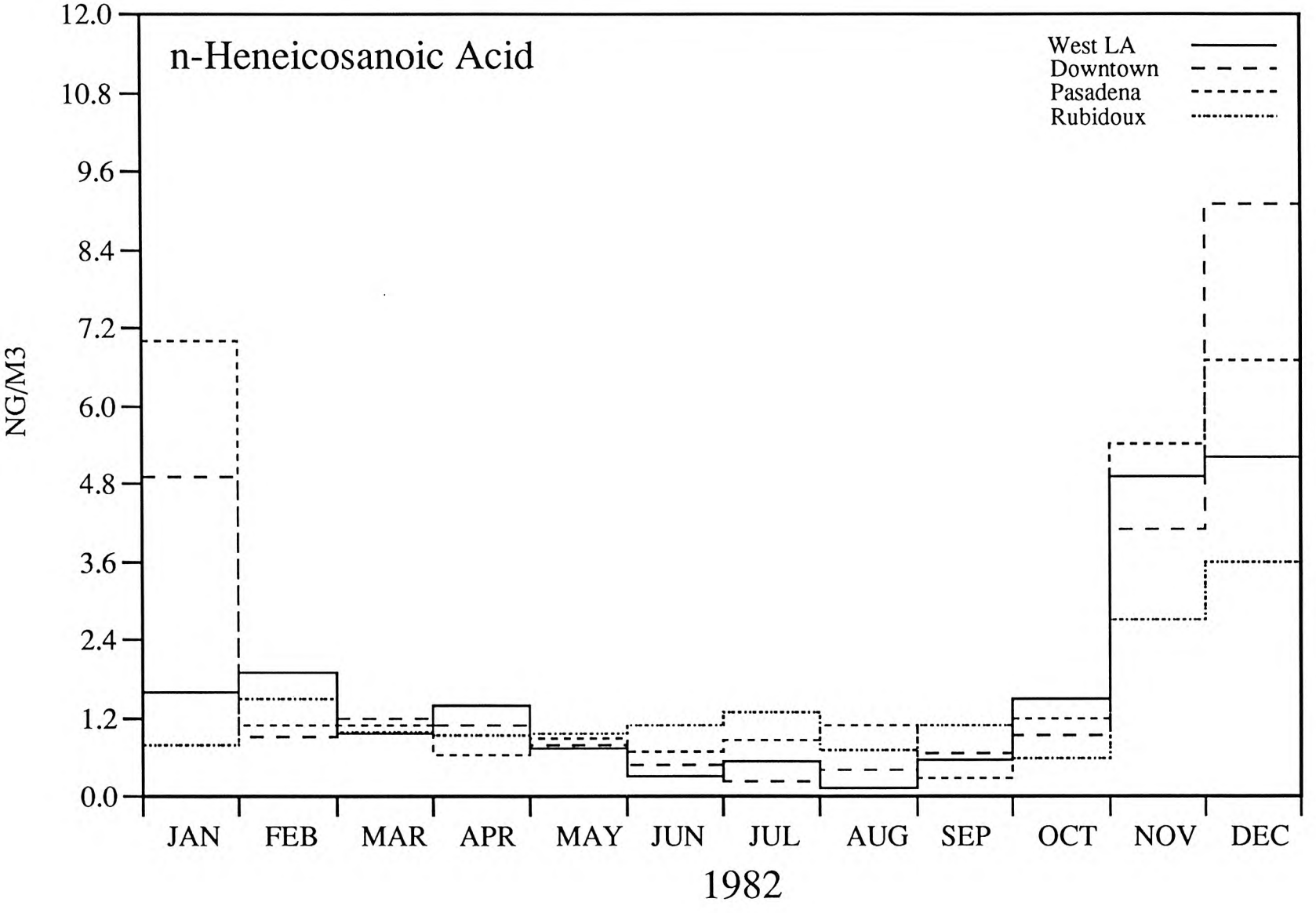

n-Hexadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
360.0
324.0
288.0
252.0
216.0
180.0
144.0
108.0
72.0
36.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

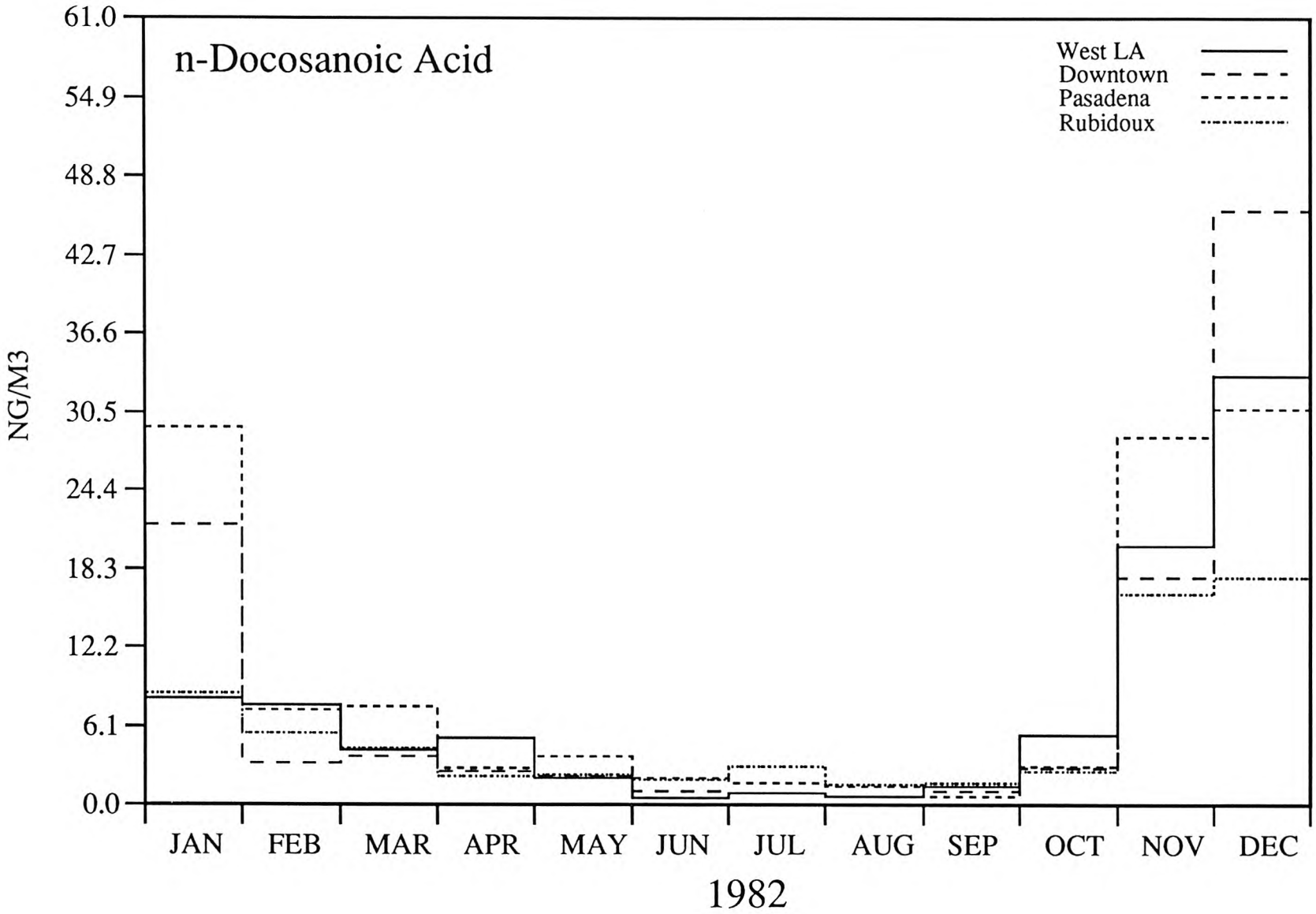

n-Heptadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
15.0
13.5
12.0
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

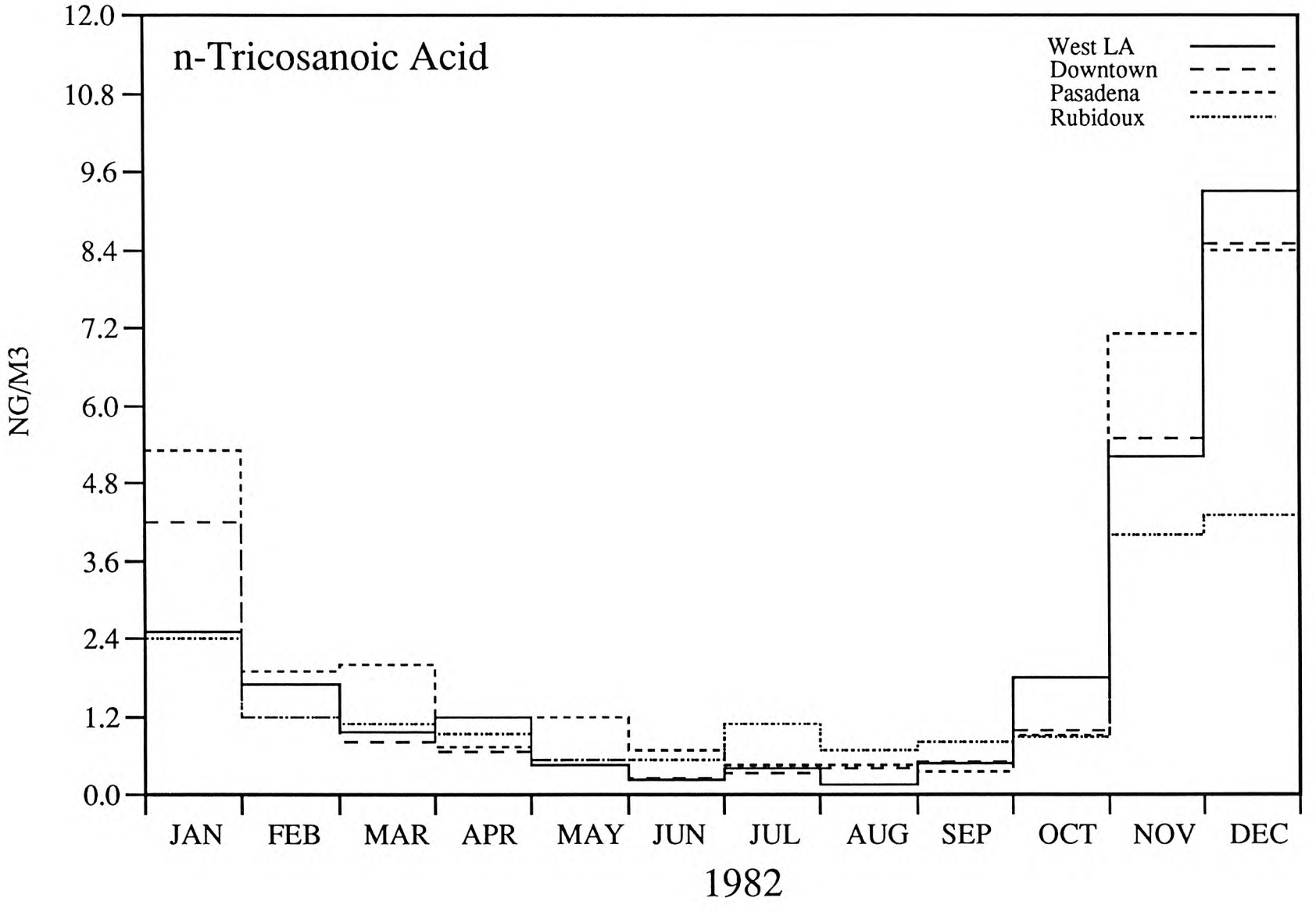

n-Octadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
140.0
126.0
112.0
98.0
84.0
70.0
56.0
42.0
28.0
14.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

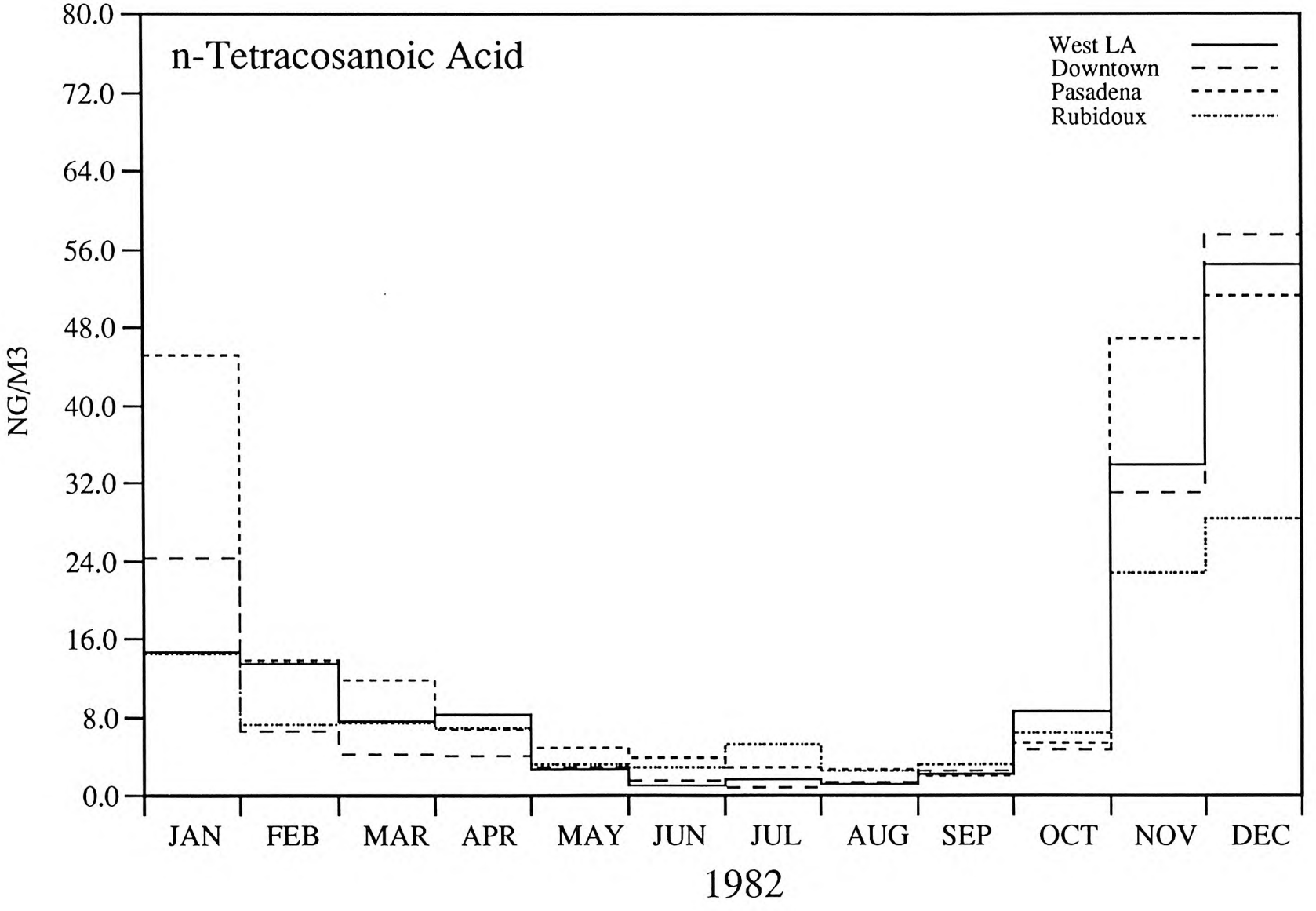

n-Nonadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

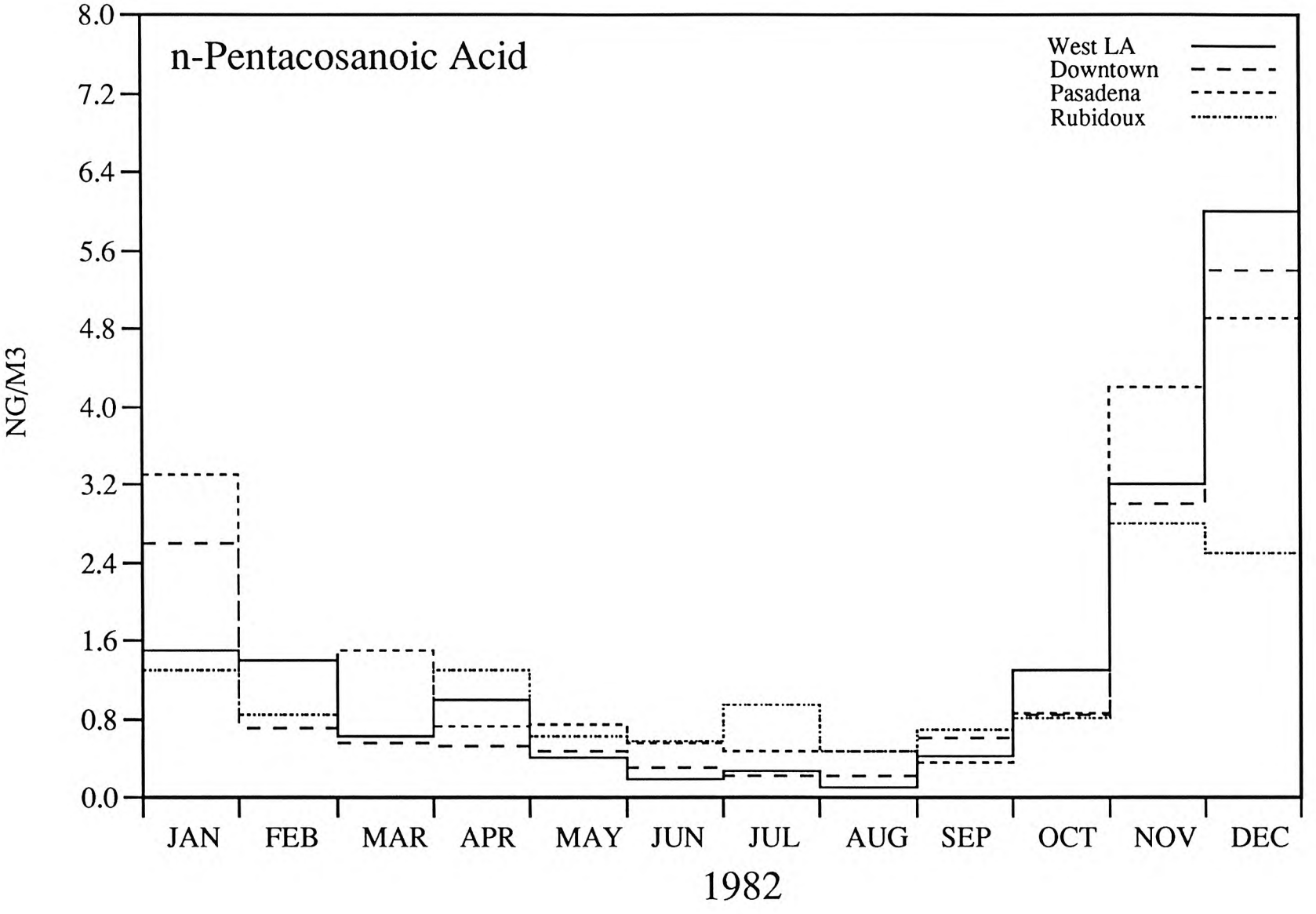

n-Eicosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
28.0
25.2
22.4
19.6
16.8
14.0
11.2
8.4
5.6
2.8
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

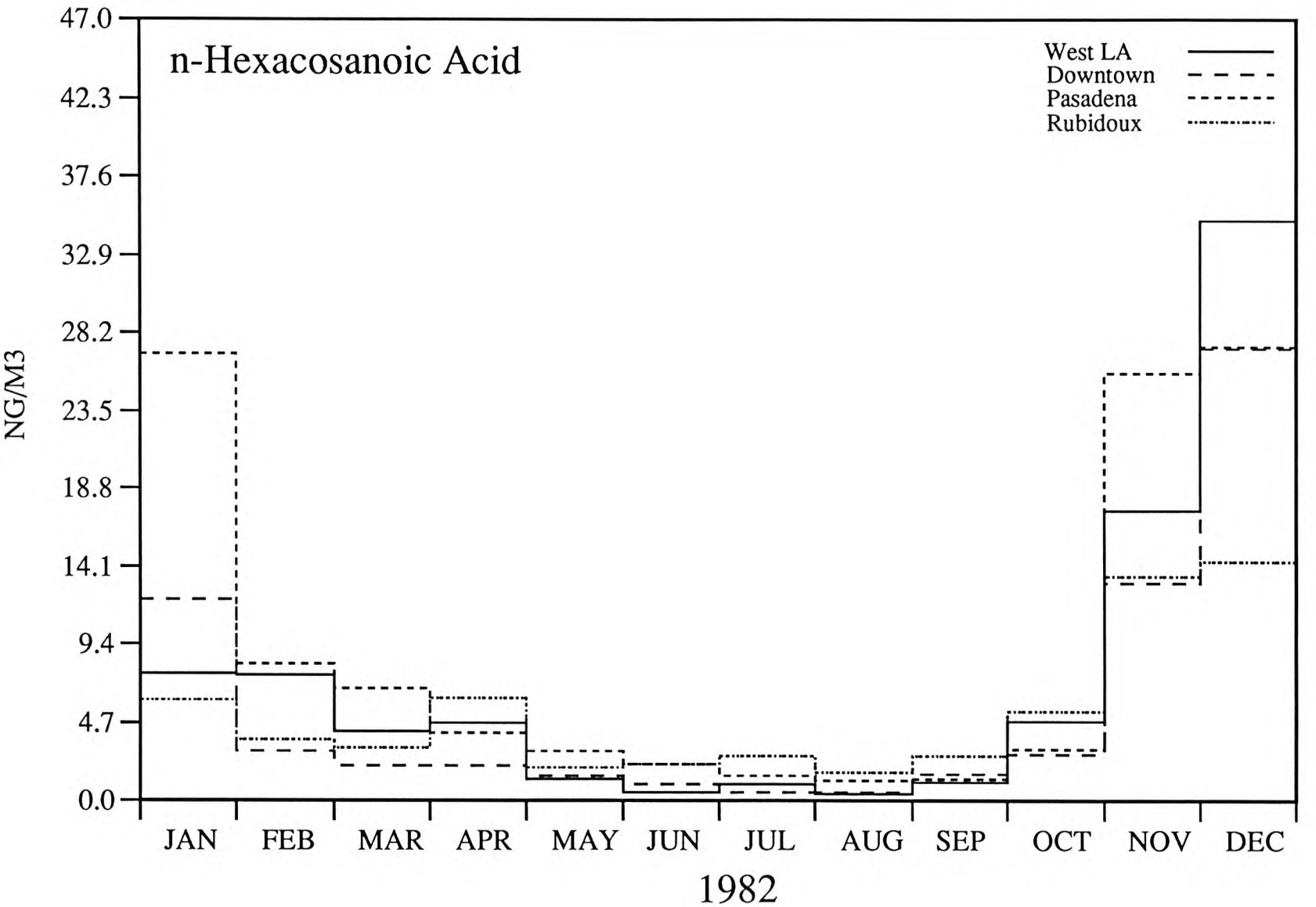

n-Heneicosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
12.0
10.8
9.6
8.4
7.2
6.0
4.8
3.6
2.4
1.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

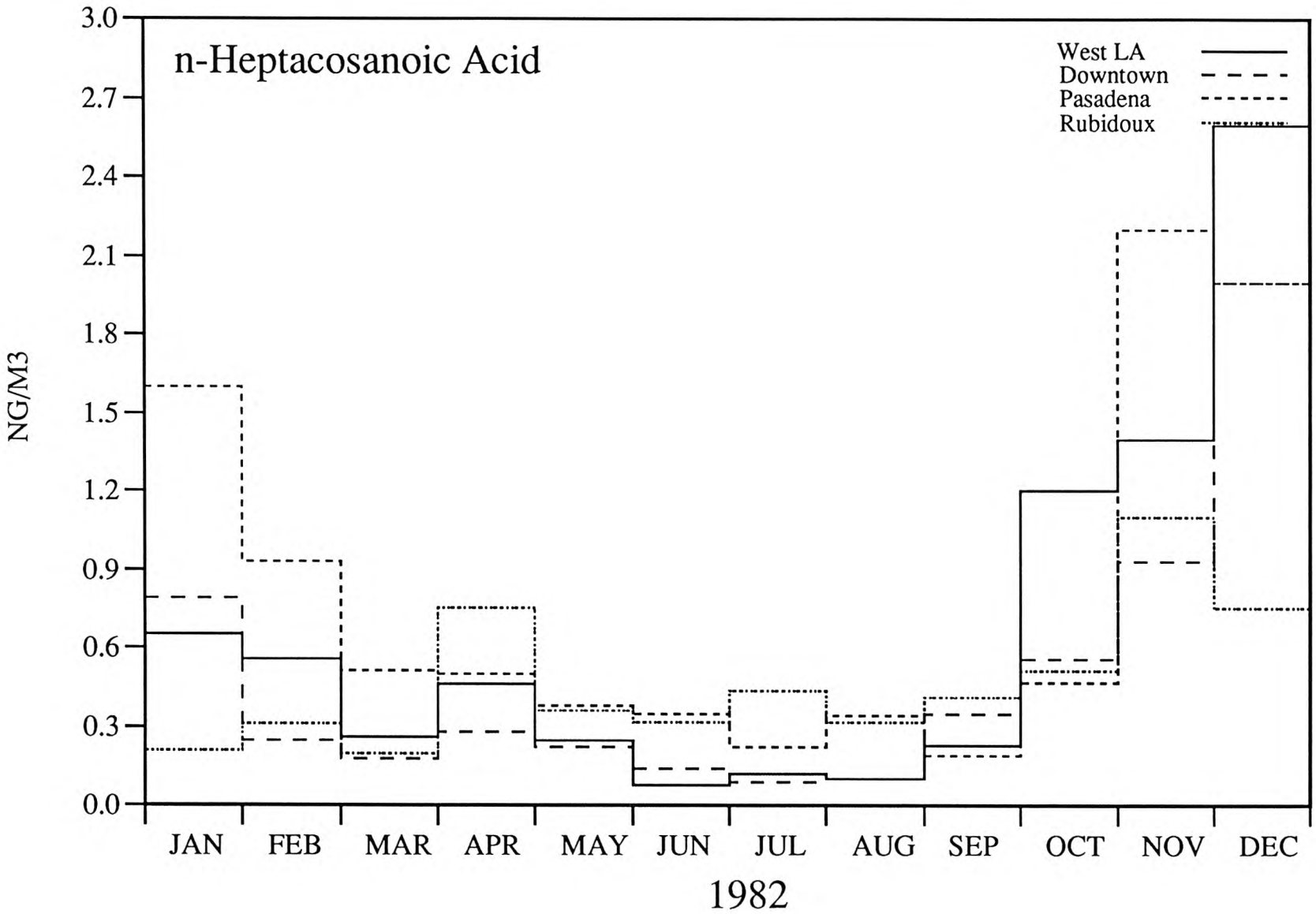

n-Docosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
61.0
54.9
48.8
42.7
36.6
30.5
24.4
18.3
12.2
6.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

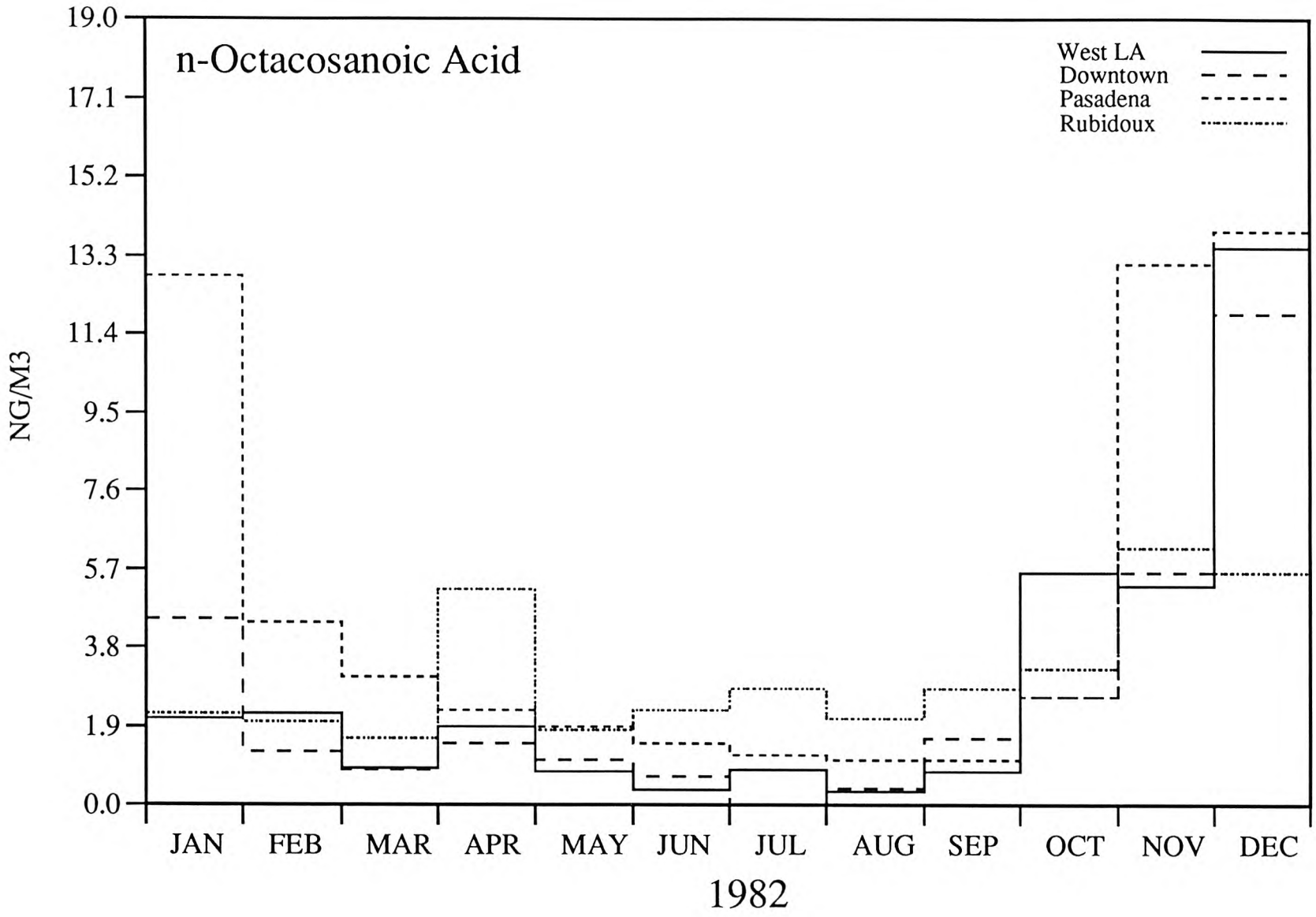

n-Tricosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
12.0
10.8
9.6
8.4
7.2
6.0
4.8
3.6
2.4
1.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

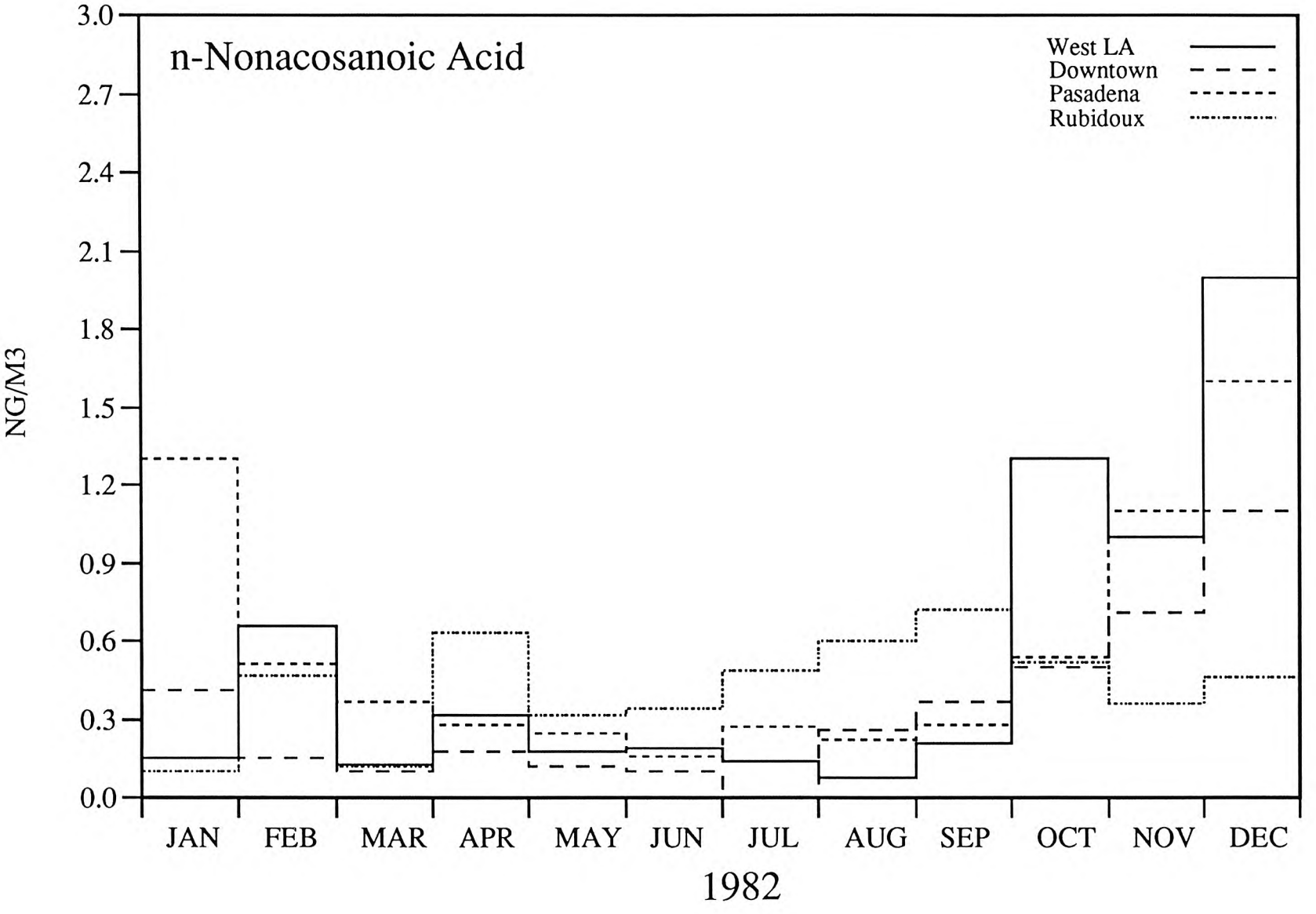

n-Tetracosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
80.0
72.0
64.0
56.0
48.0
40.0
32.0
24.0
16.0
8.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

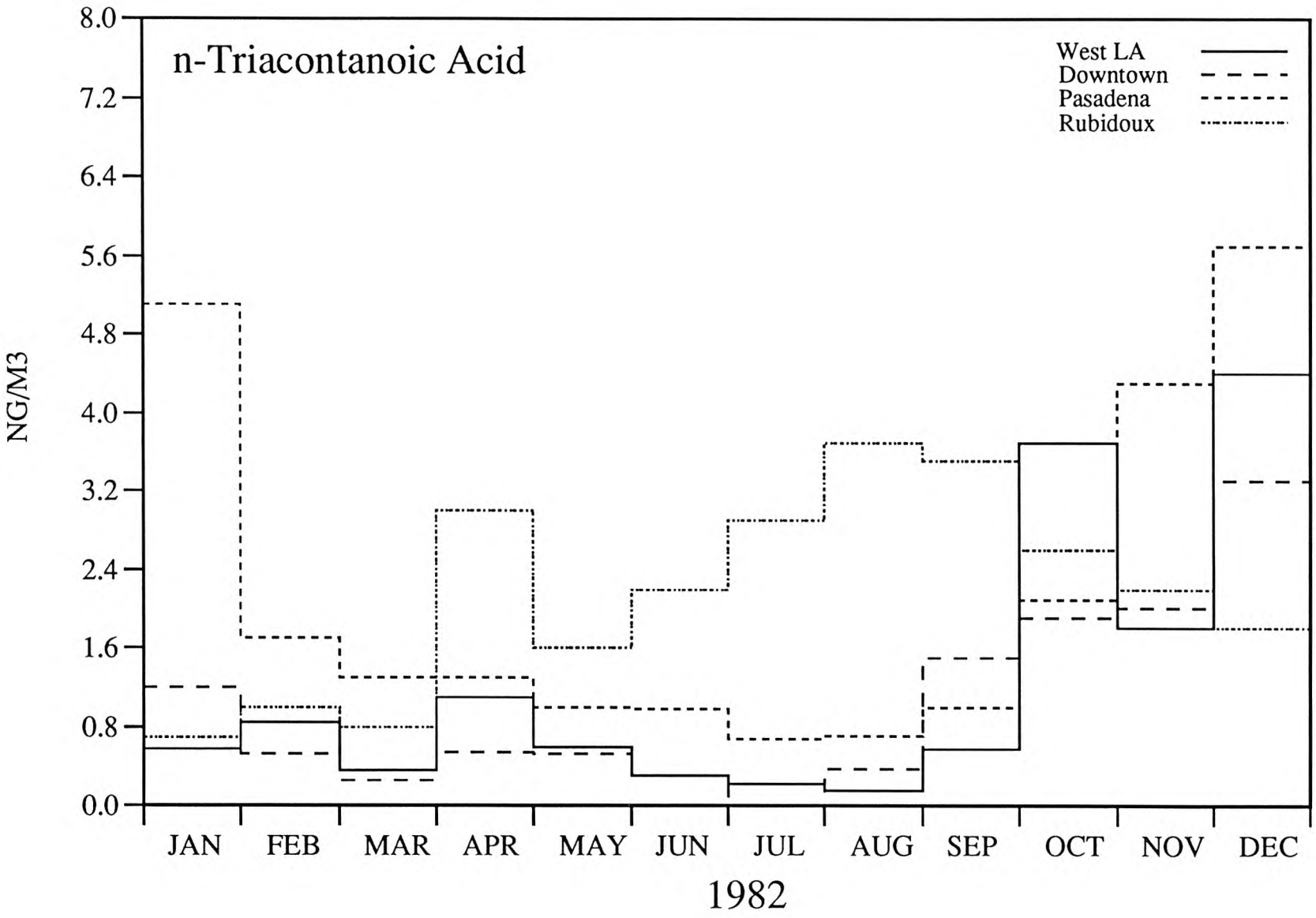

n-Pentacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
8.0
7.2
6.4
5.6
4.8
4.0
3.2
2.4
1.6
0.8
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Hexacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
47.0
42.3
37.6
32.9
28.2
23.5
18.8
14.1
9.4
4.7
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Heptacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

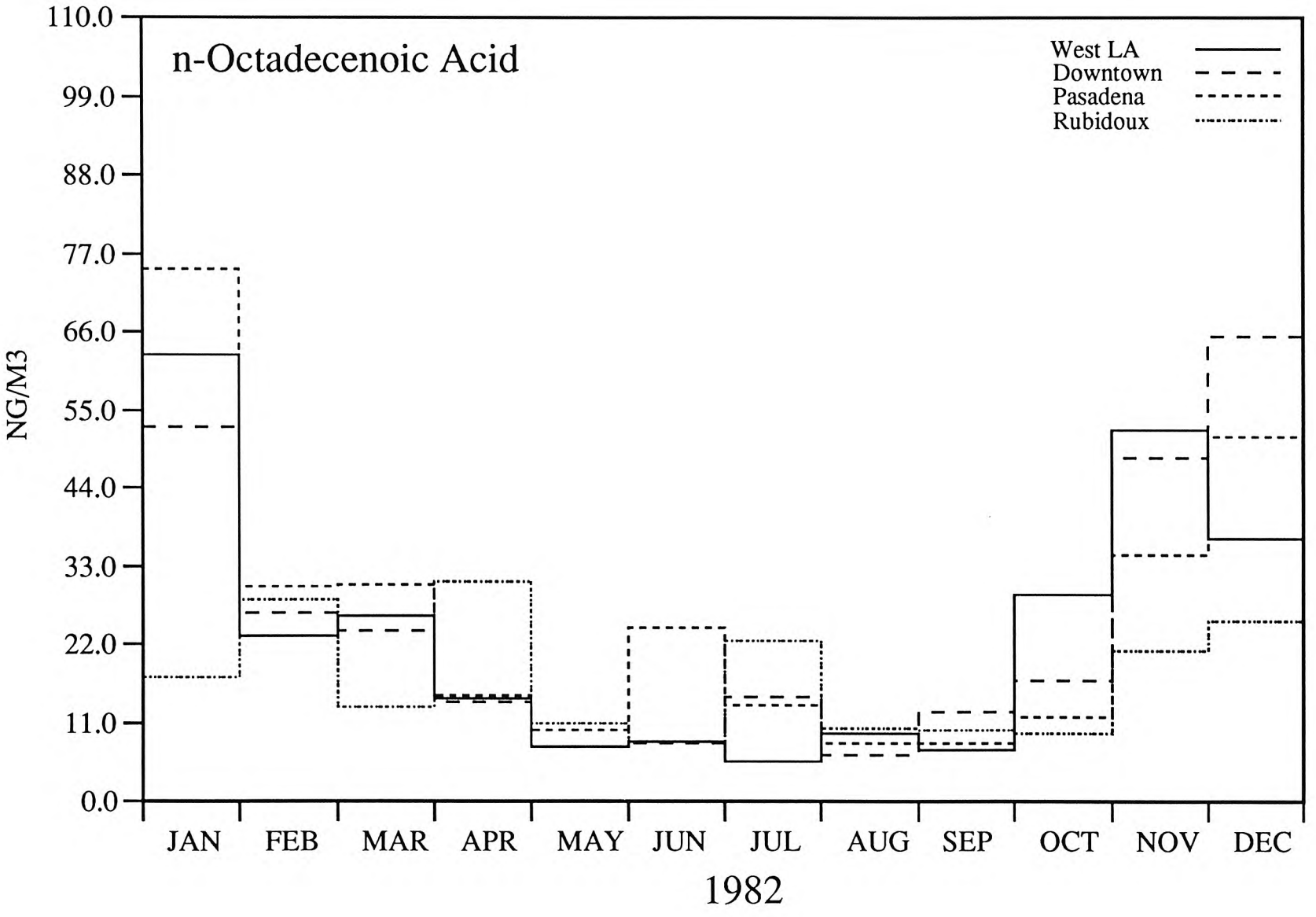

n-Octacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
19.0
17.1
15.2
13.3
11.4
9.5
7.6
5.7
3.8
1.9
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Nonacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Triacontanoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
8.0
7.2
6.4
5.6
4.8
4.0
3.2
2.4
1.6
0.8
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

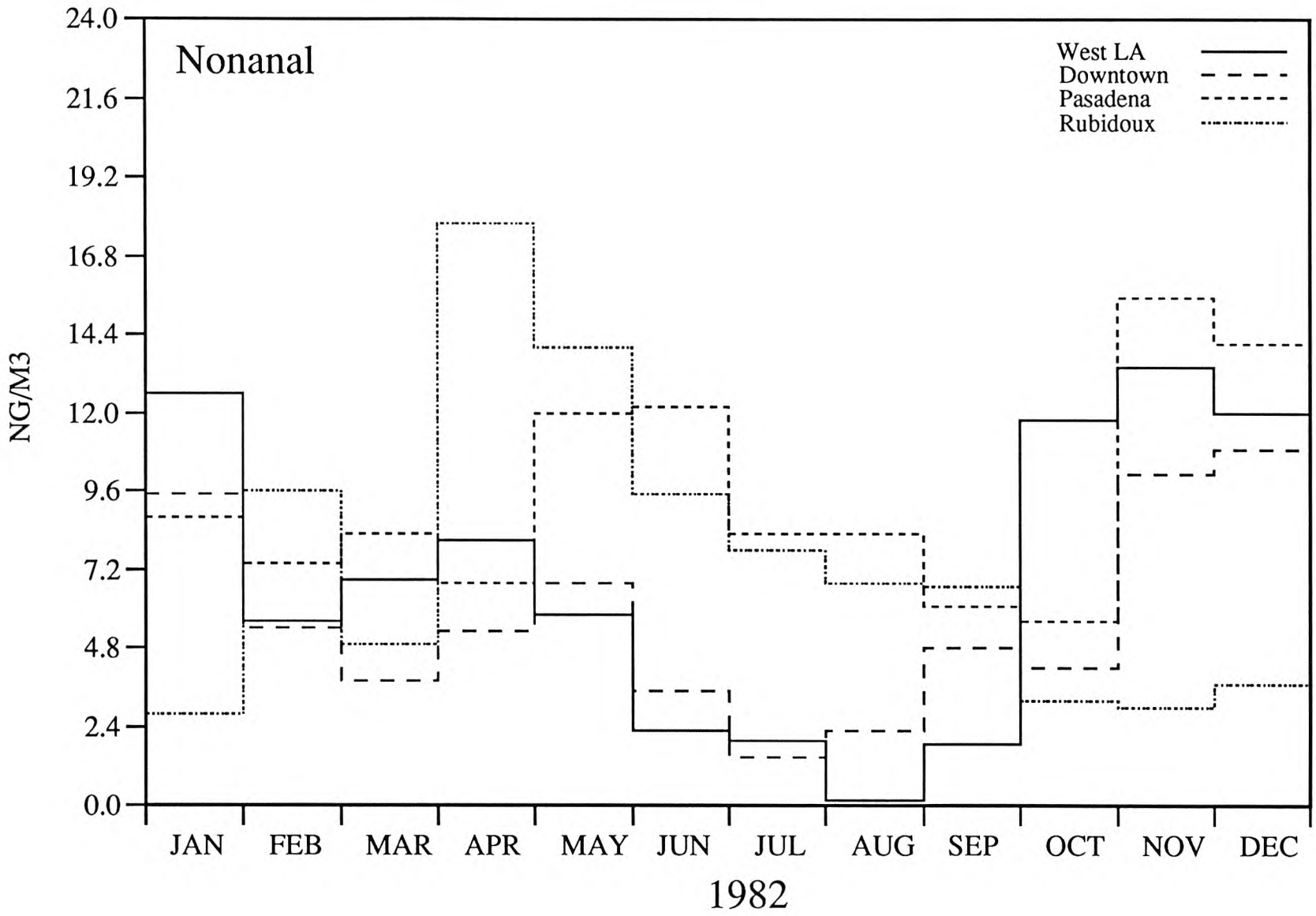
Appendix A3

Ambient Concentration Profiles for n-Alkenoic Acids


n-Octadecenoic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
110.0
99.0
88.0
77.0
66.0
55.0
44.0
33.0
22.0
11.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

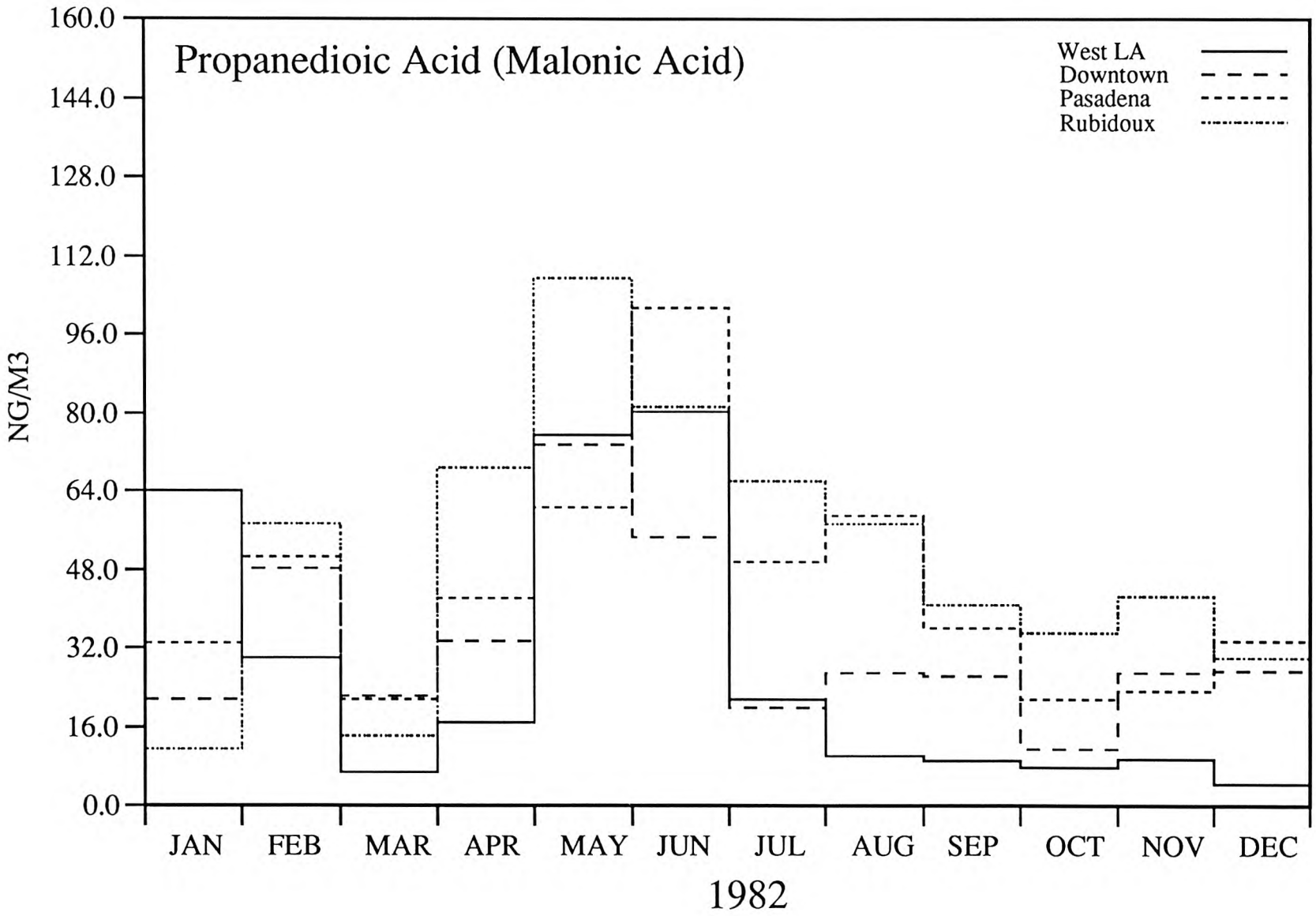
Appendix A4

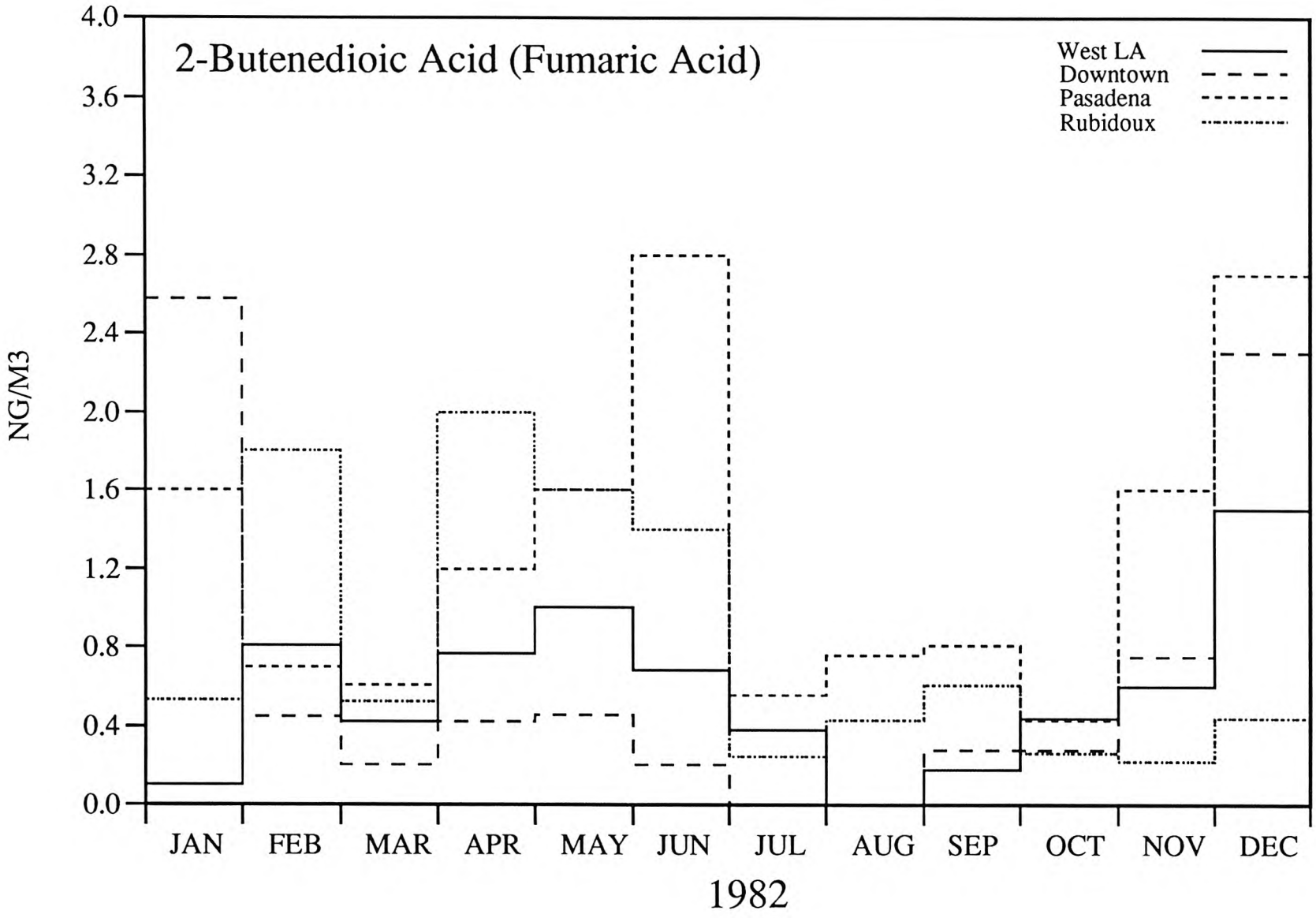
Ambient Concentration Profiles for n-Alkanals

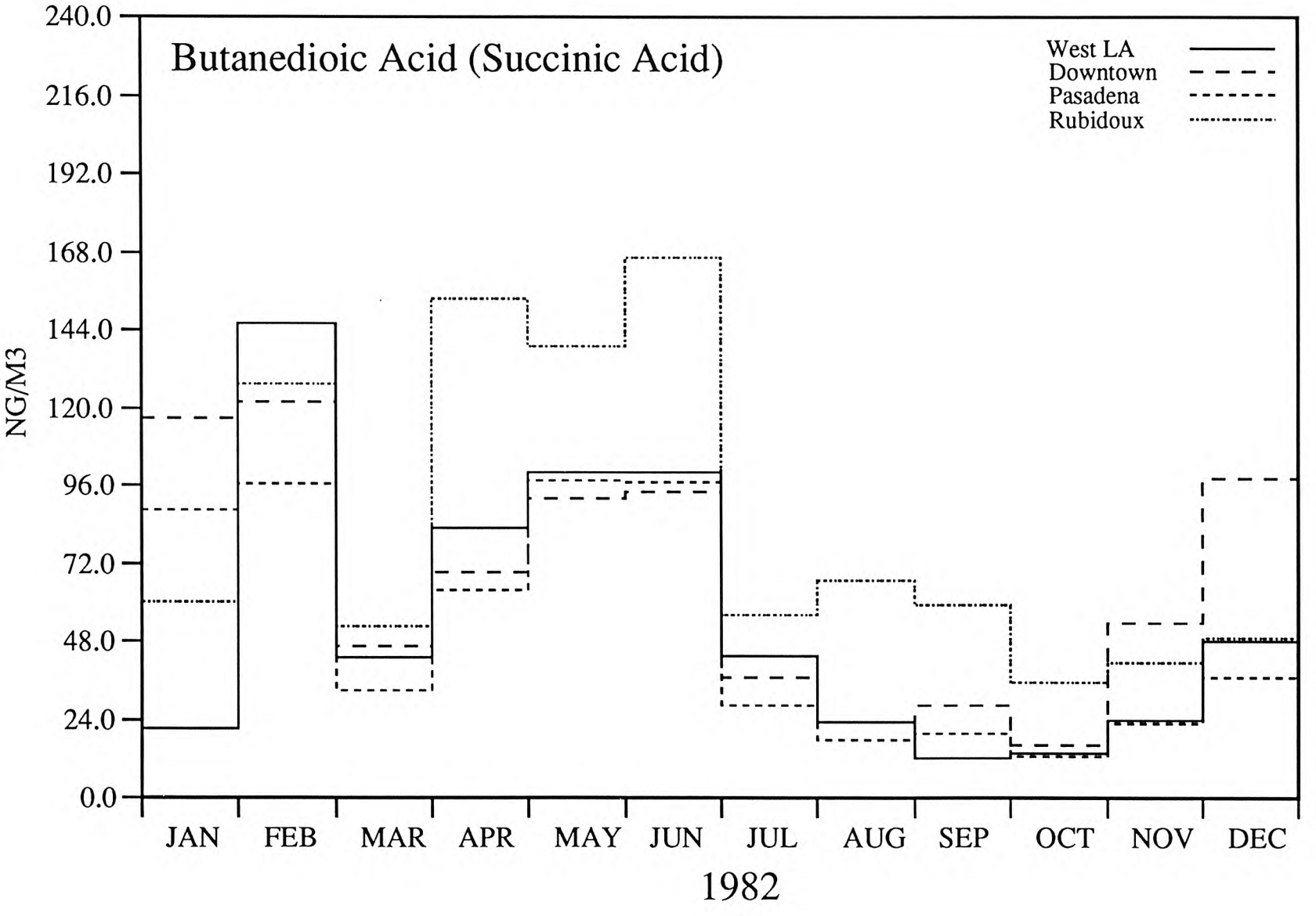

Nonanal
West LA
Downtown
Pasadena
Rubidoux
NG/M3
24.0
21.6
19.2
16.8
14.4
12.0
9.6
7.2
4.8
2.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

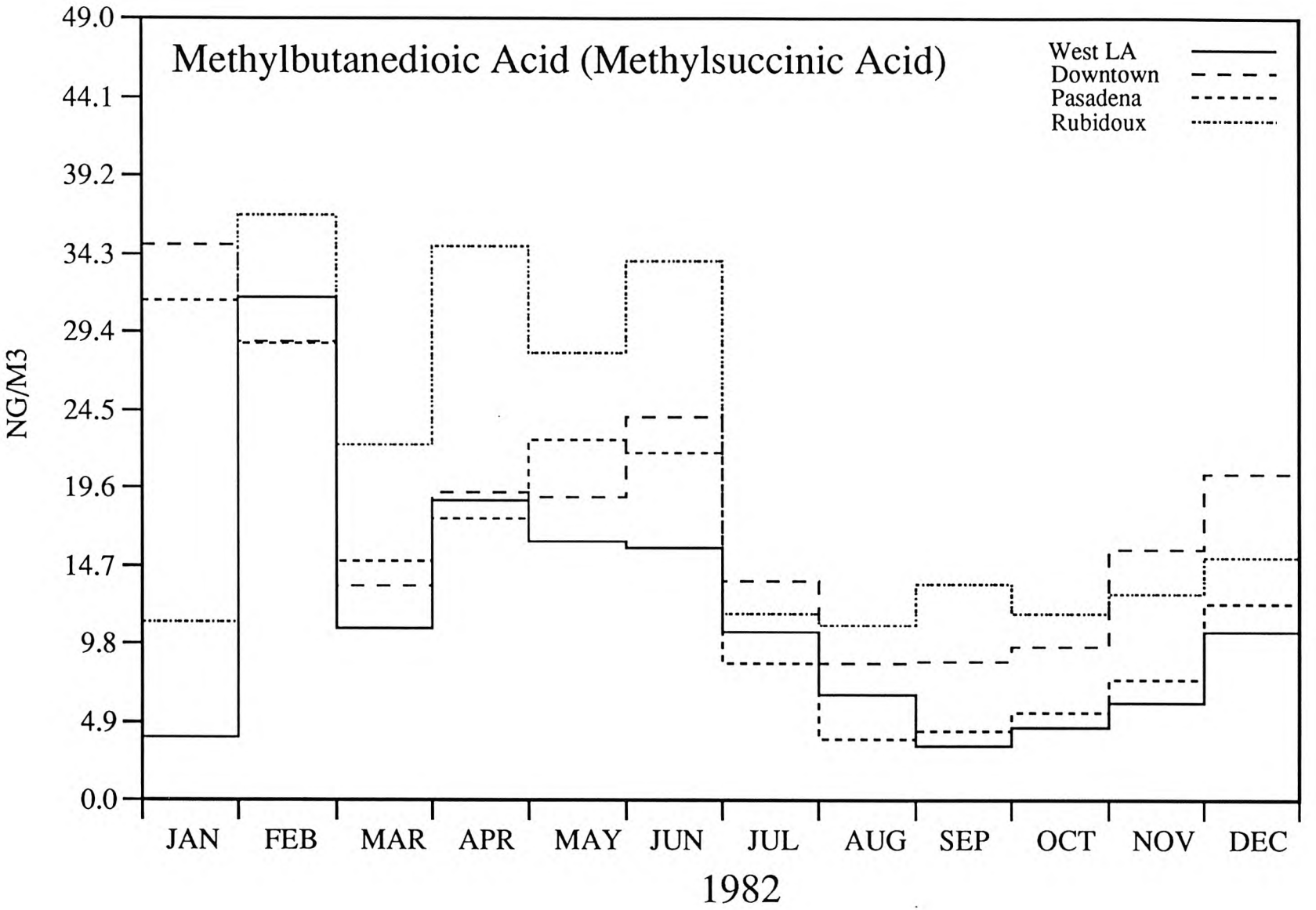
Appendix A5

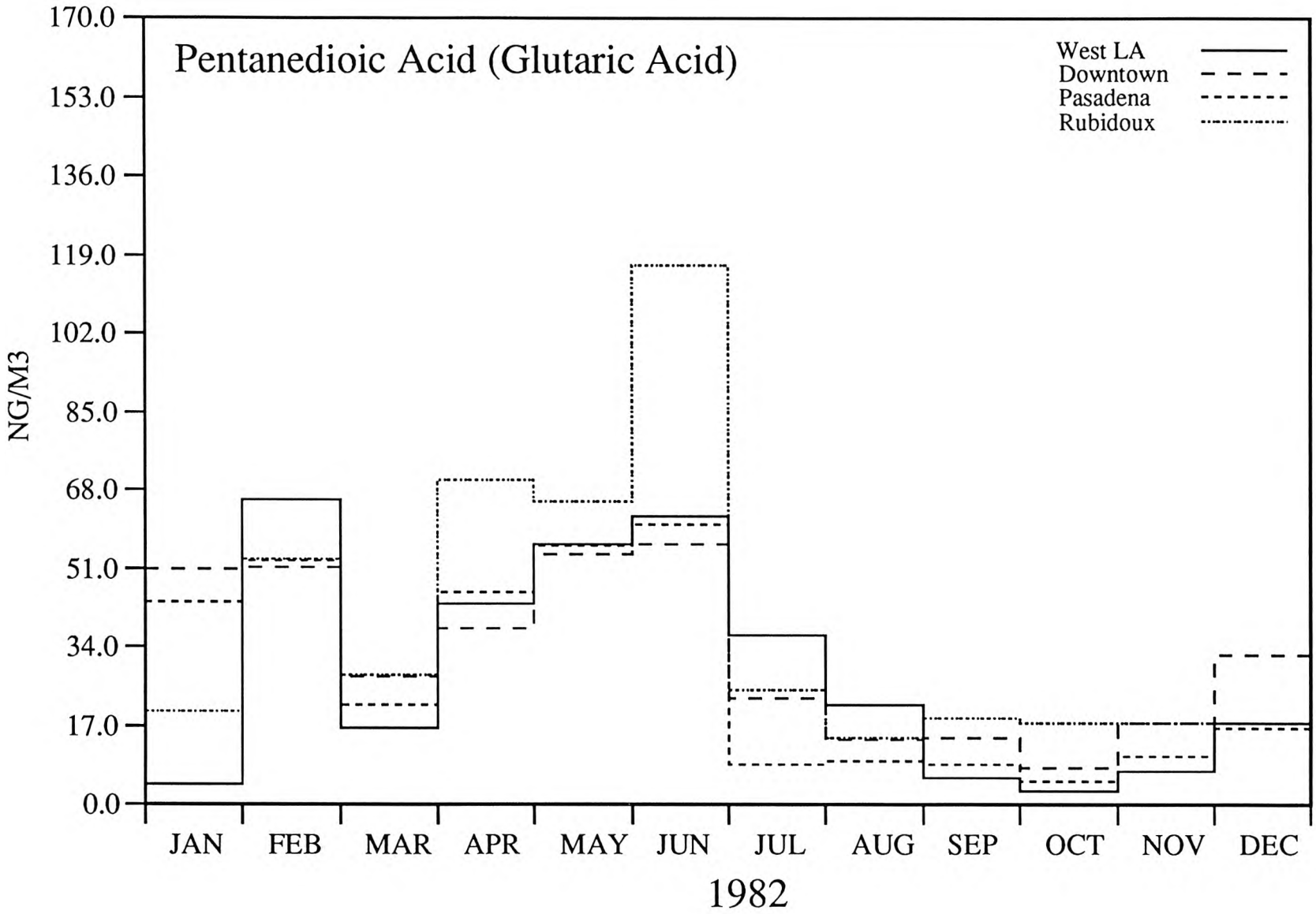
Ambient Concentration Profiles for Aliphatic Dicarboxylic Acids

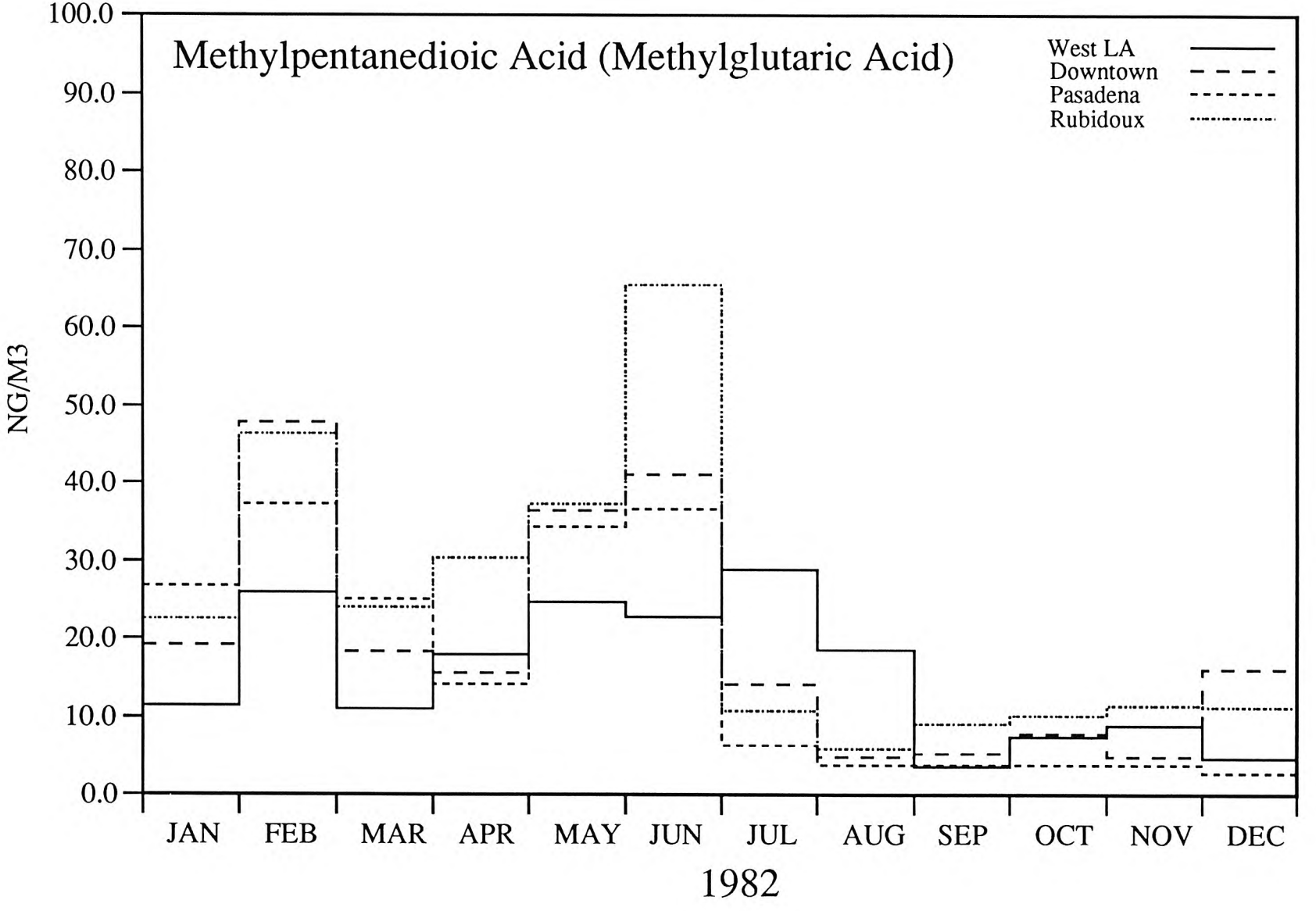

Propanedioic Acid (Malonic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
160.0
144.0
128.0
112.0
96.0
80.0
64.0
48.0
32.0
16.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


2-Butenedioic Acid (Fumaric Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Butanedioic Acid (Succinic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
240.0
216.0
192.0
168.0
144.0
120.0
96.0
72.0
48.0
24.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Methylbutanedioic Acid (Methylsuccinic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
49.0
44.1
39.2
34.3
29.4
24.5
19.6
14.7
9.8
4.9
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Pentanedioic Acid (Glutaric Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
170.0
153.0
136.0
119.0
102.0
85.0
68.0
51.0
34.0
17.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Methylpentanedioic Acid (Methylglutaric Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
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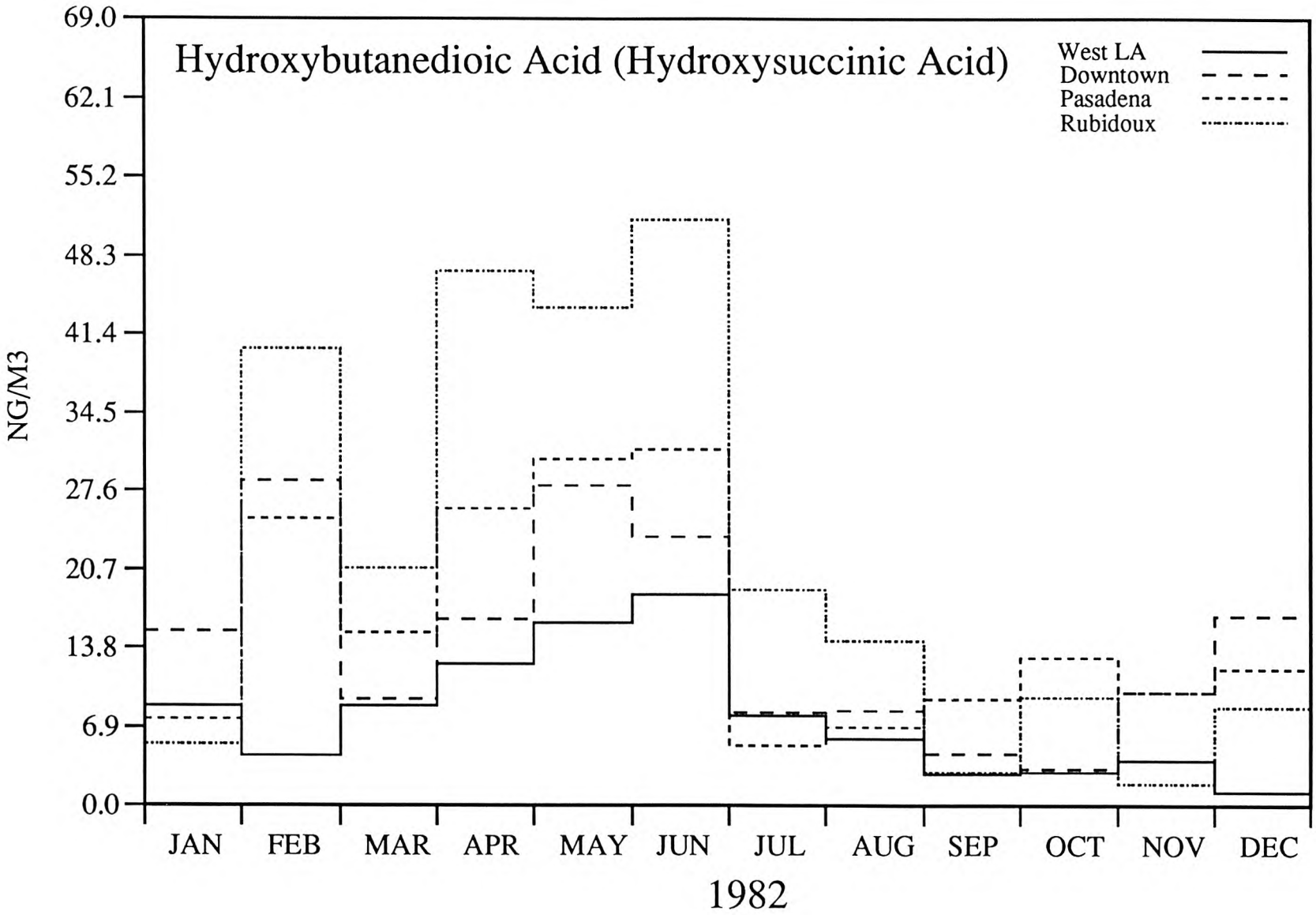
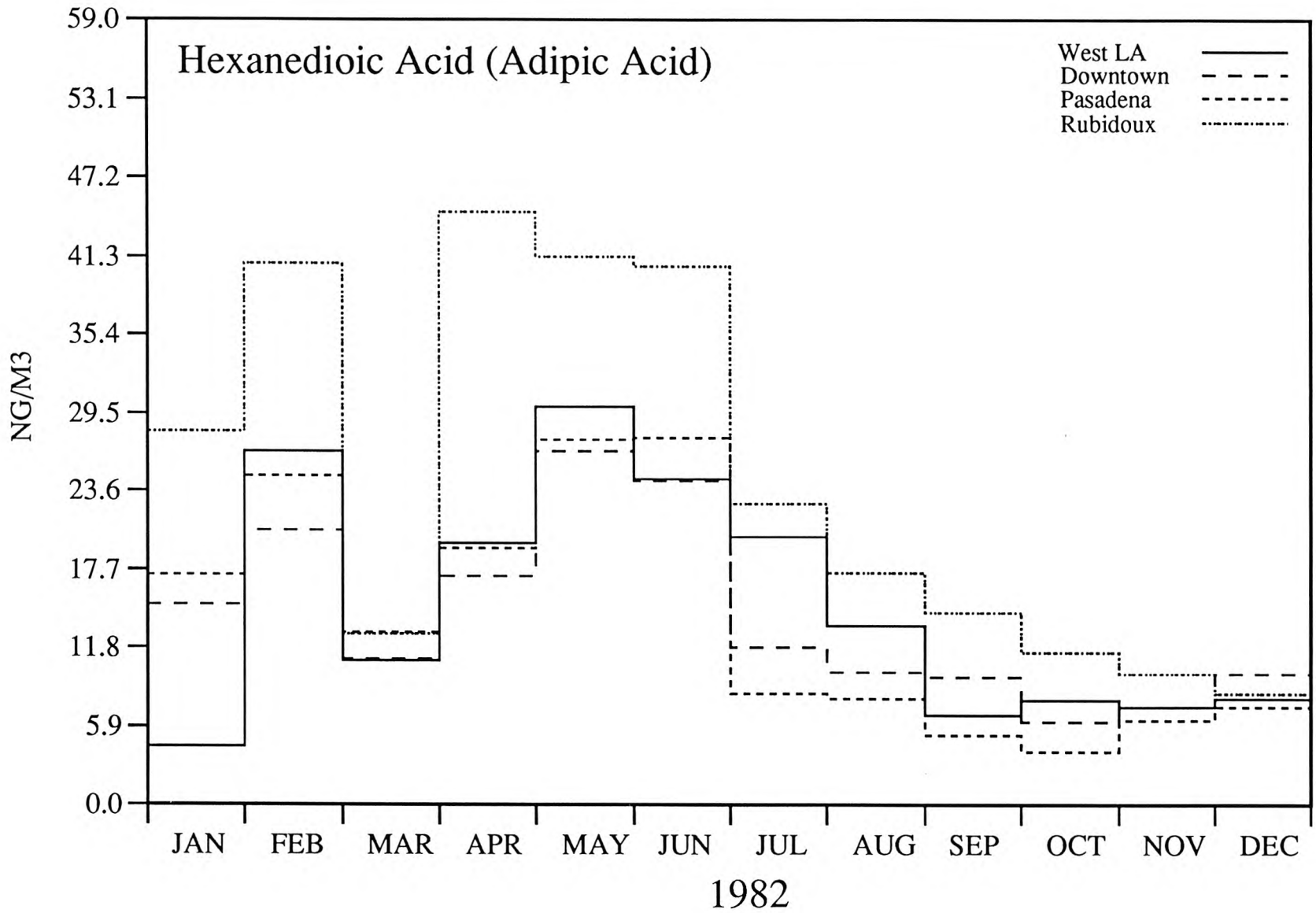
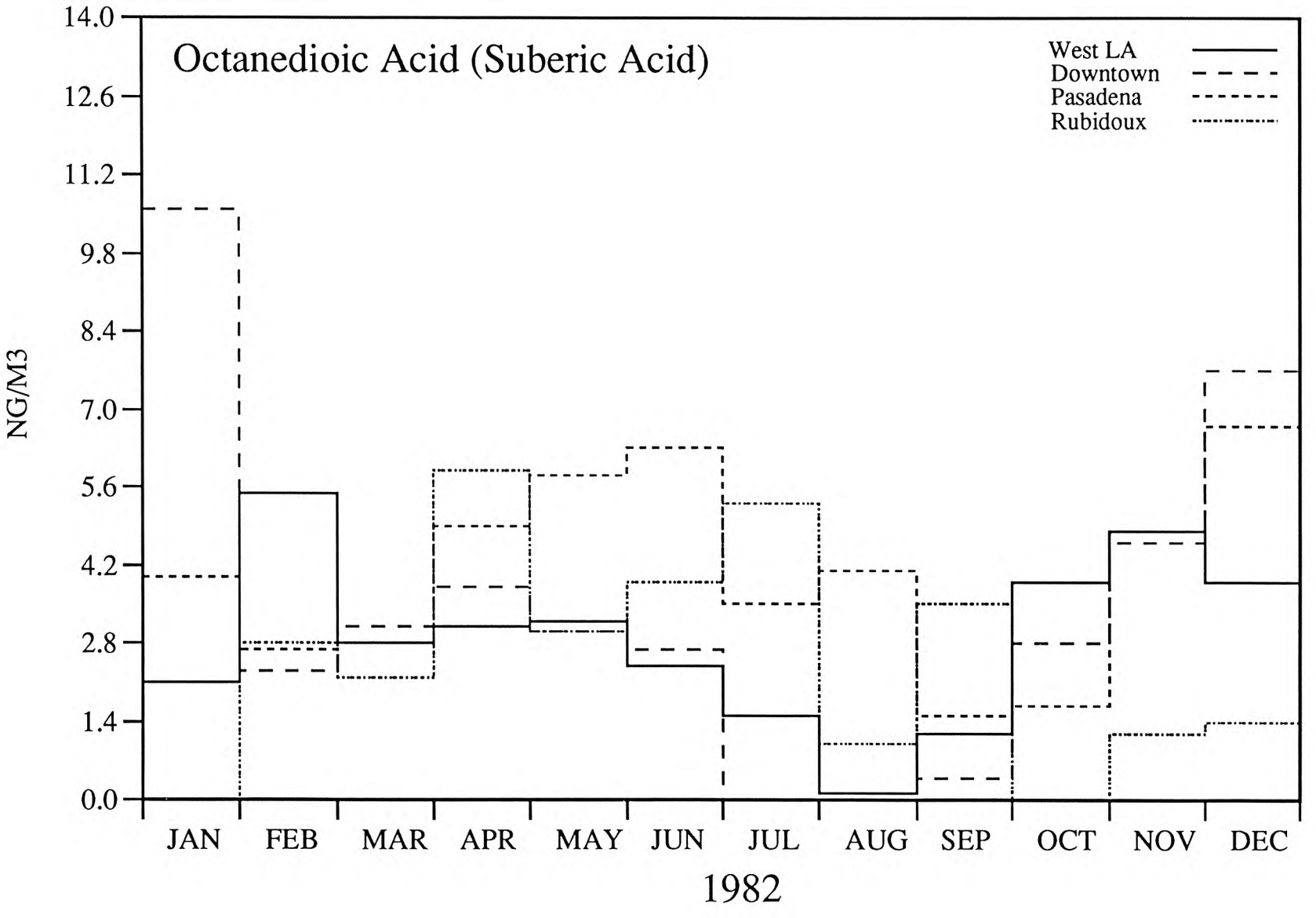
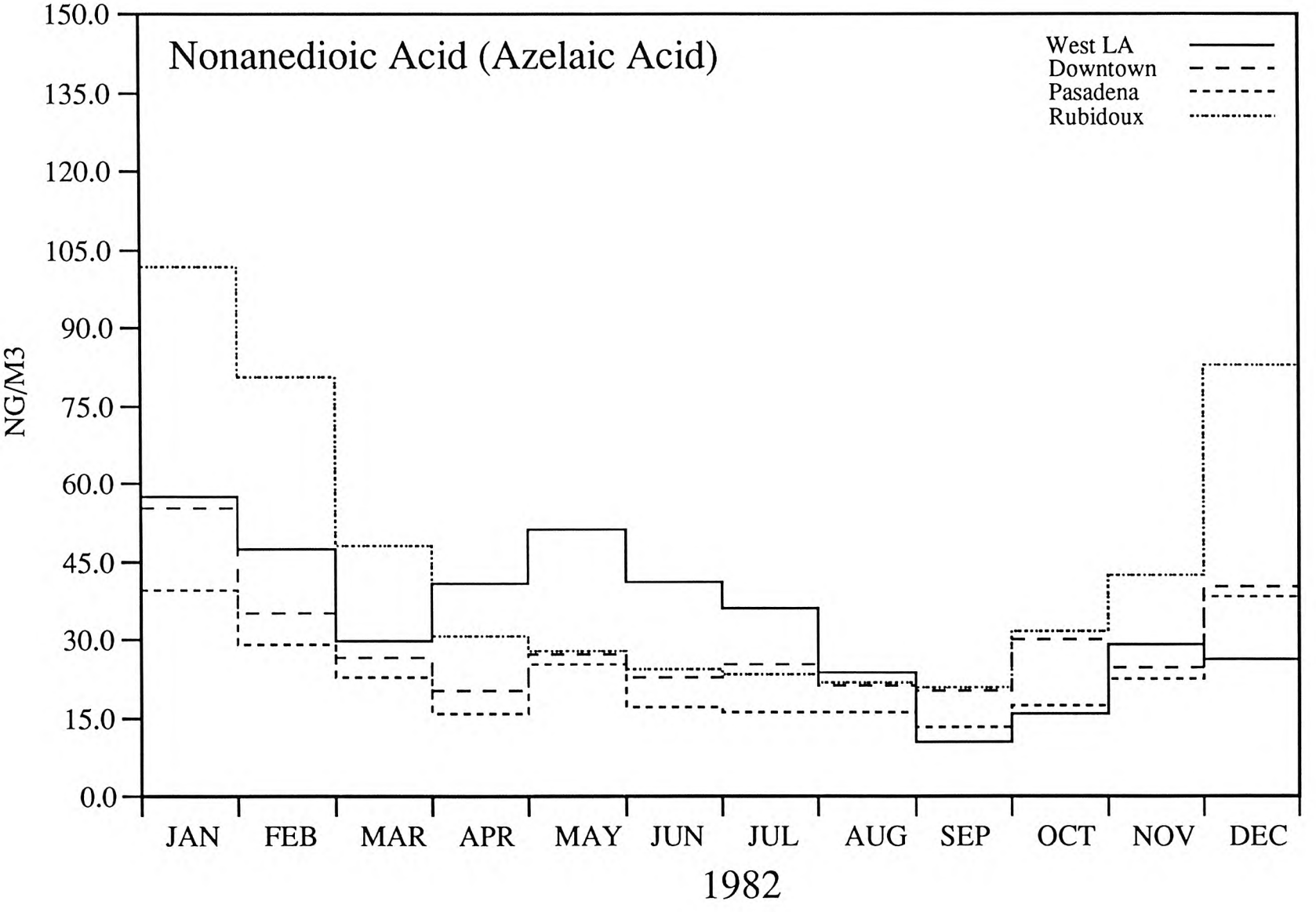
NOV
DEC
1982


Hydroxybutanedioic Acid (Hydroxysuccinic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
69.0
62.1
55.2
48.3
41.4
34.5
27.6
20.7
13.8
6.9
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

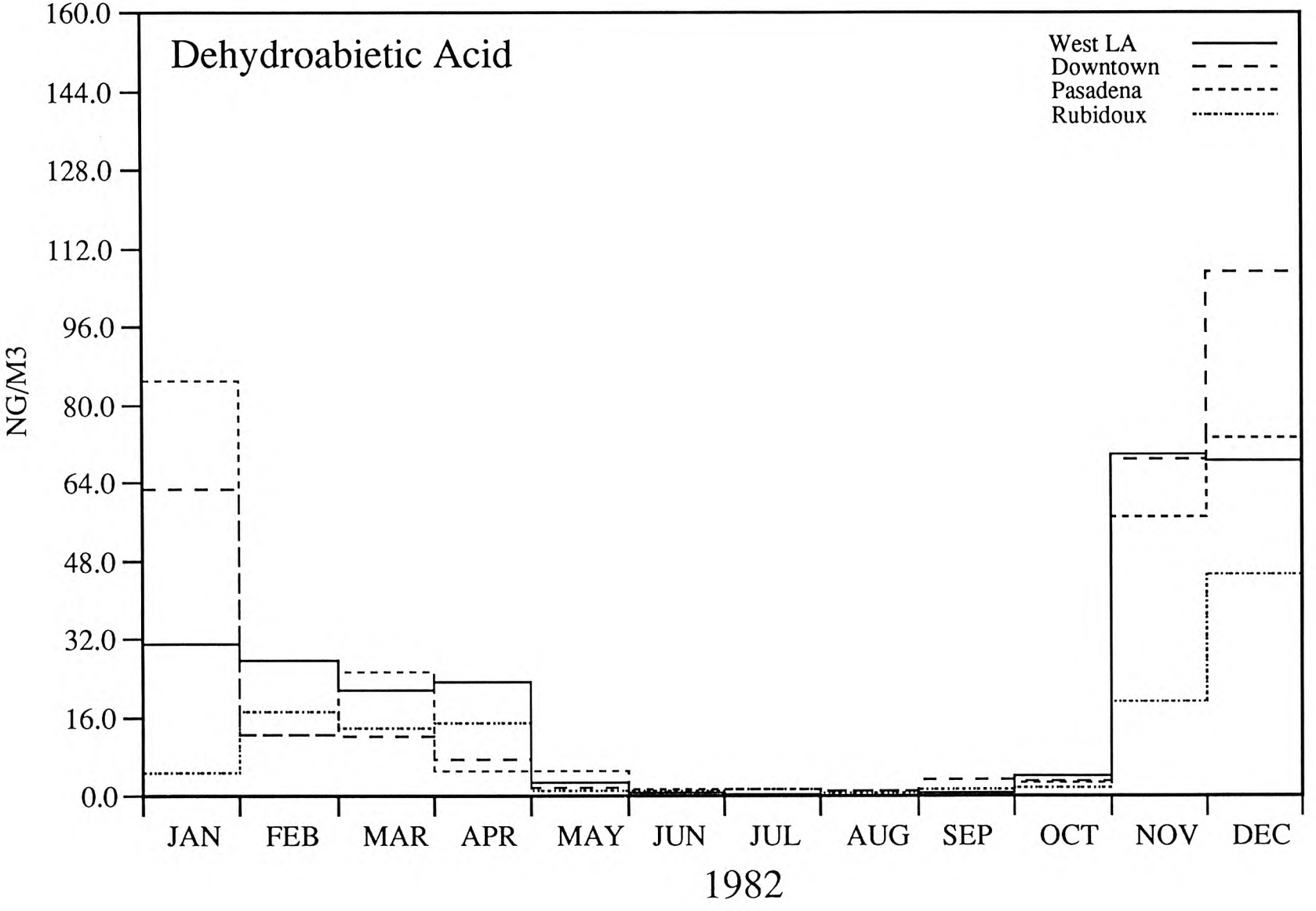

Hexanedioic Acid (Adipic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
59.0
53.1
47.2
41.3
35.4
29.5
23.6
17.7
11.8
5.9
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

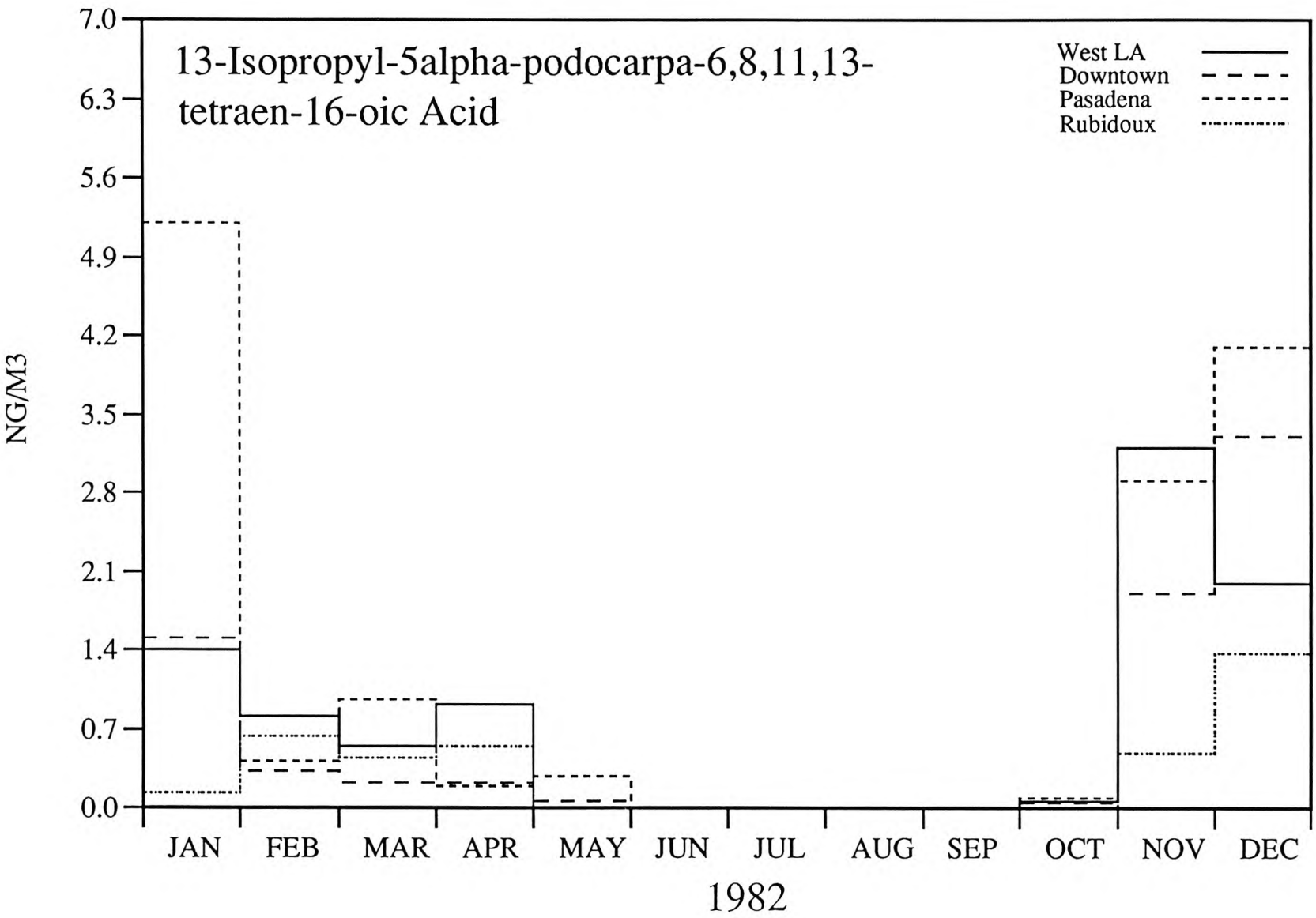

Octanedioic Acid (Suberic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
14.0
12.6
11.2
9.8
8.4
7.0
5.6
4.2
2.8
1.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

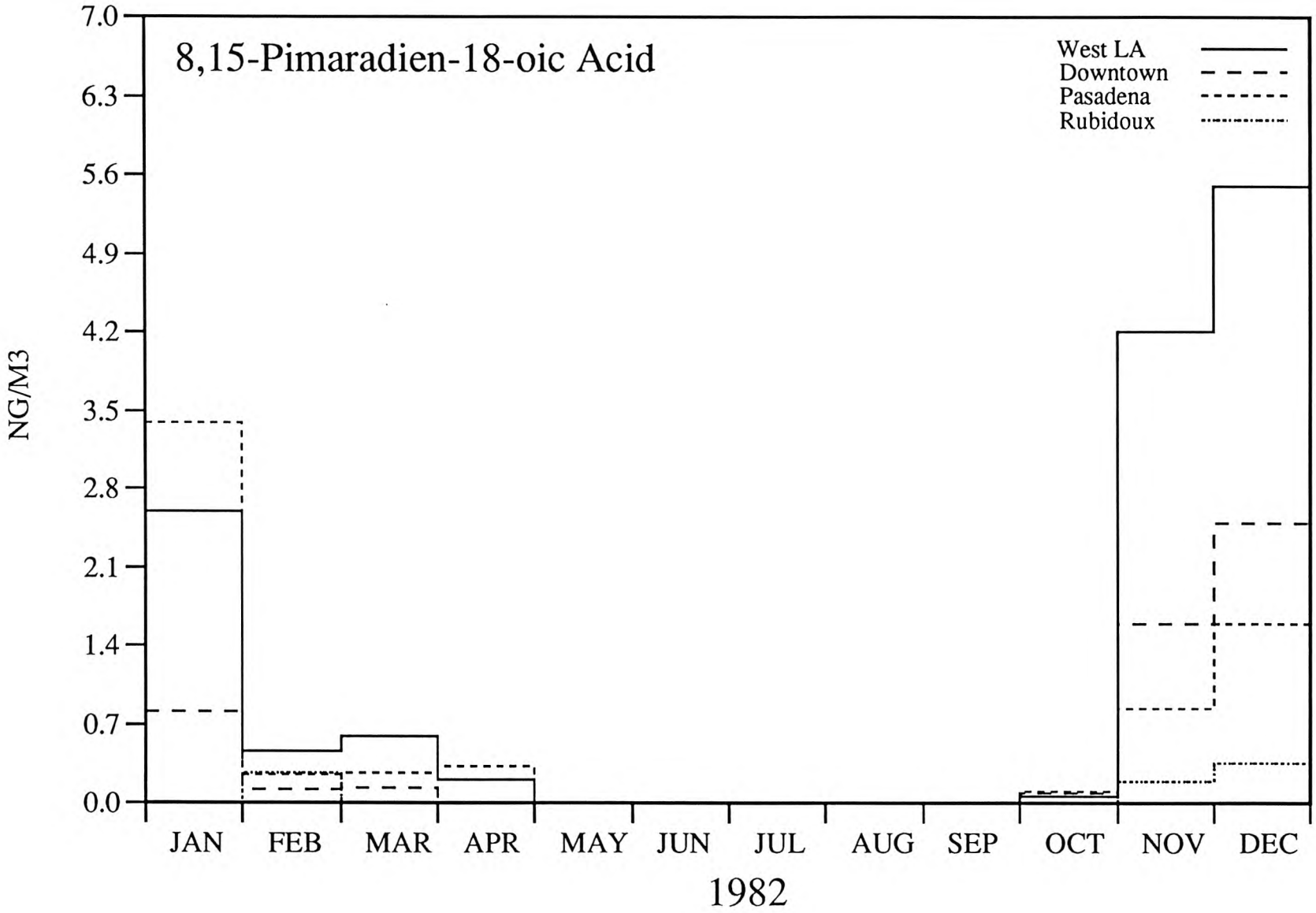

Nonanedioic Acid (Azelaic Acid)
West LA
Downtown
Pasadena
Rubidoux
NG/M3
150.0
135.0
120.0
105.0
90.0
75.0
60.0
45.0
30.0
15.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

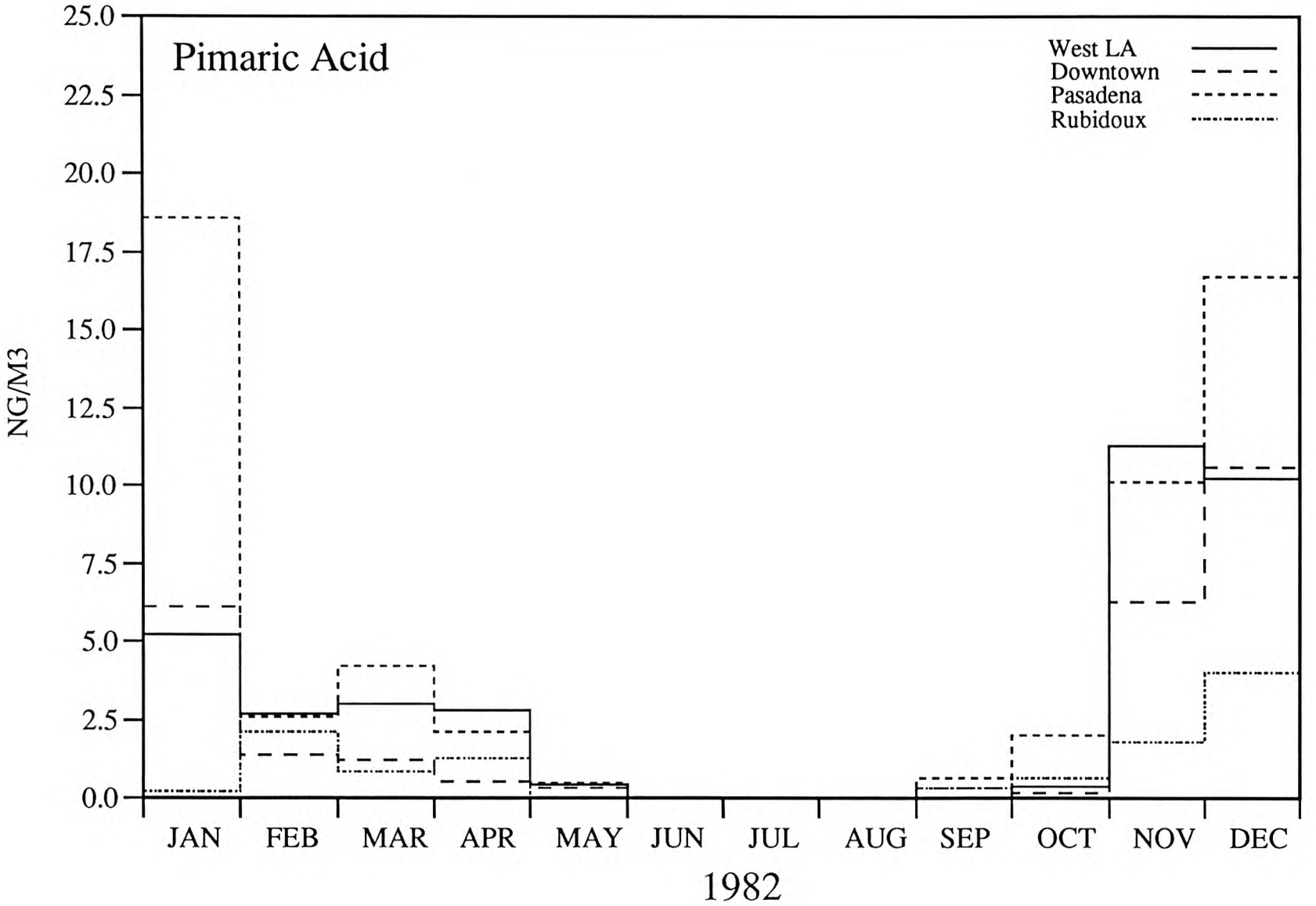
Appendix A6

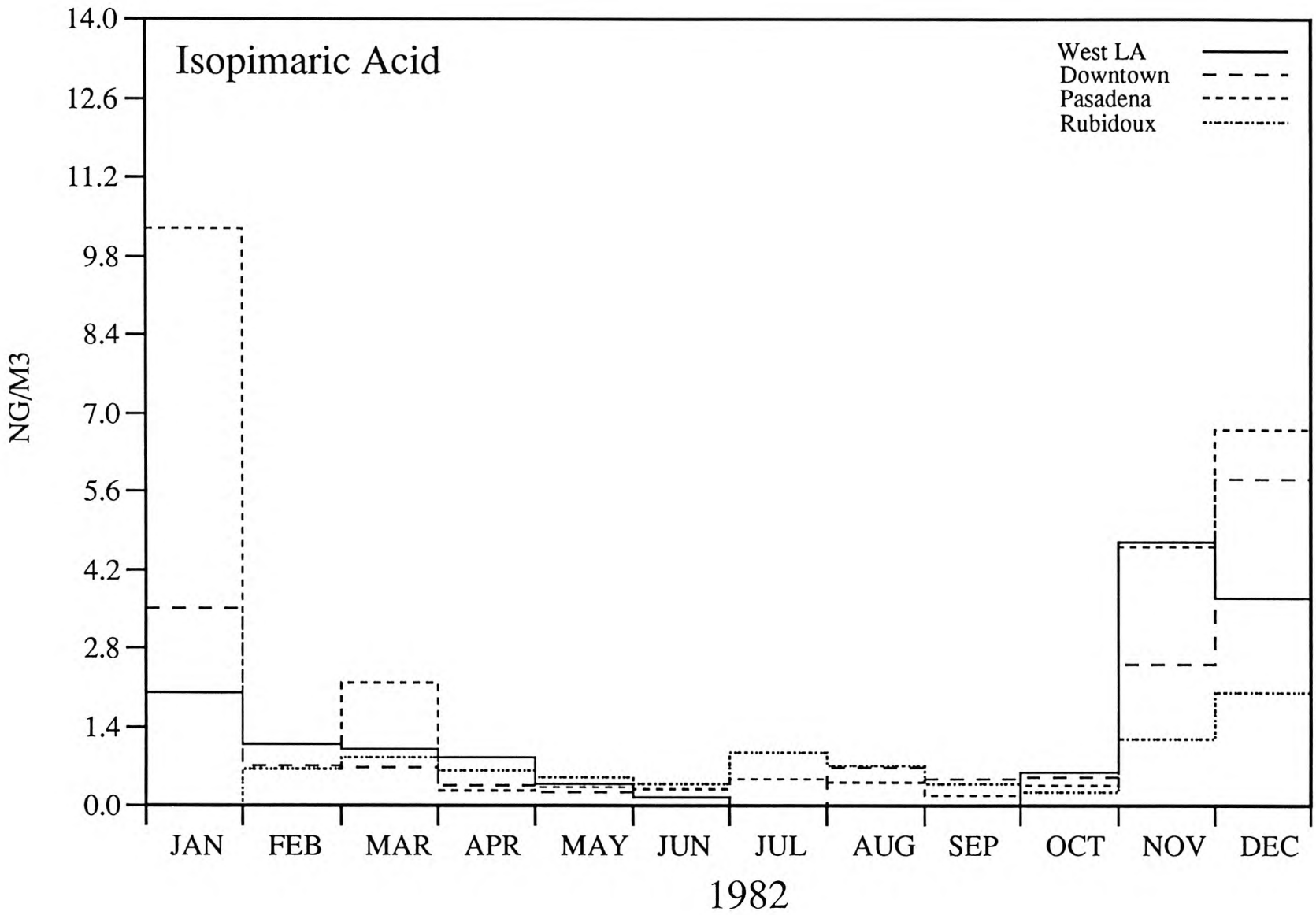
Ambient Concentration Profiles for Diterpenoid Acids and Retene

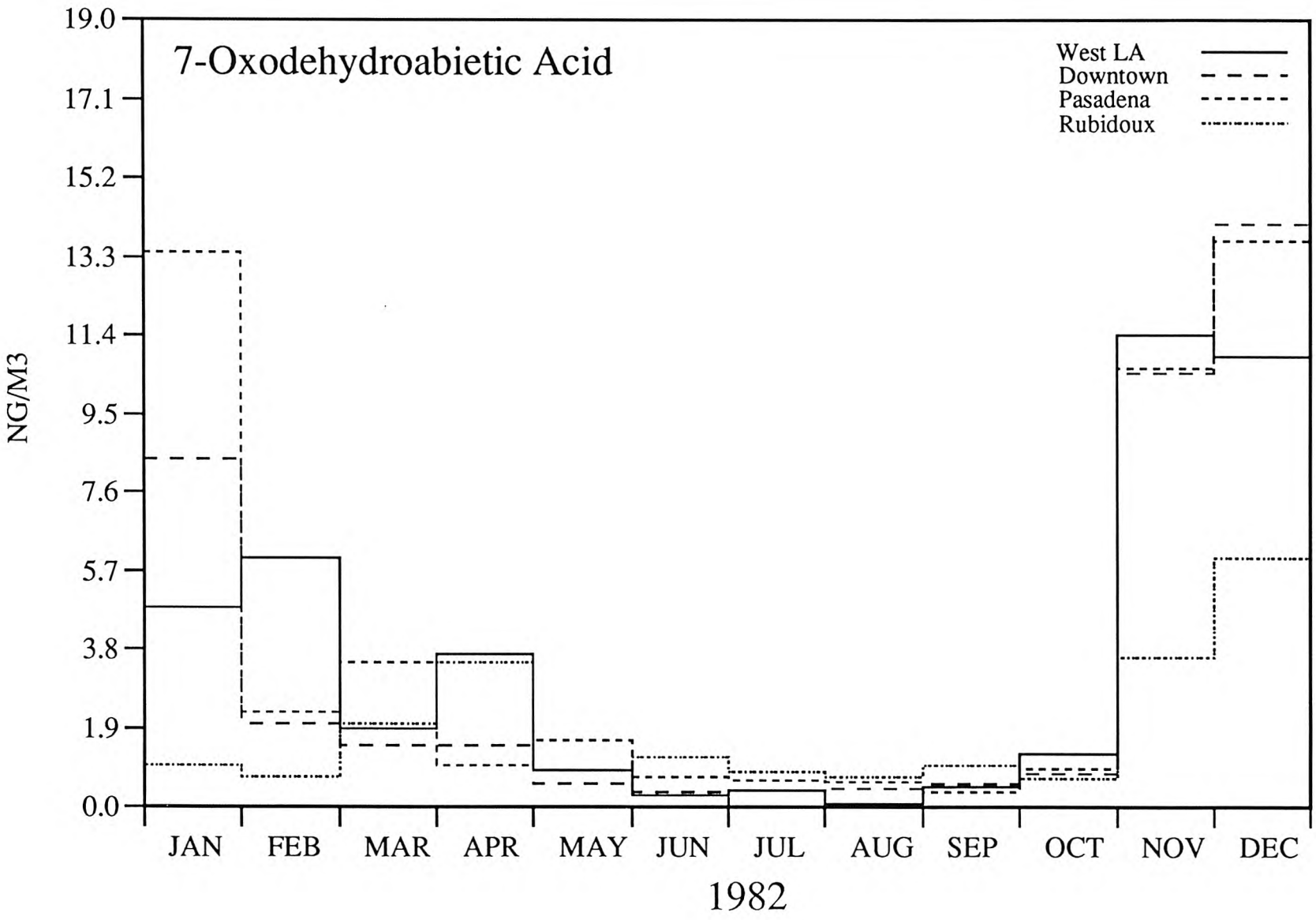

Dehydroabietic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
160.0
144.0
128.0
112.0
96.0
80.0
64.0
48.0
32.0
16.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

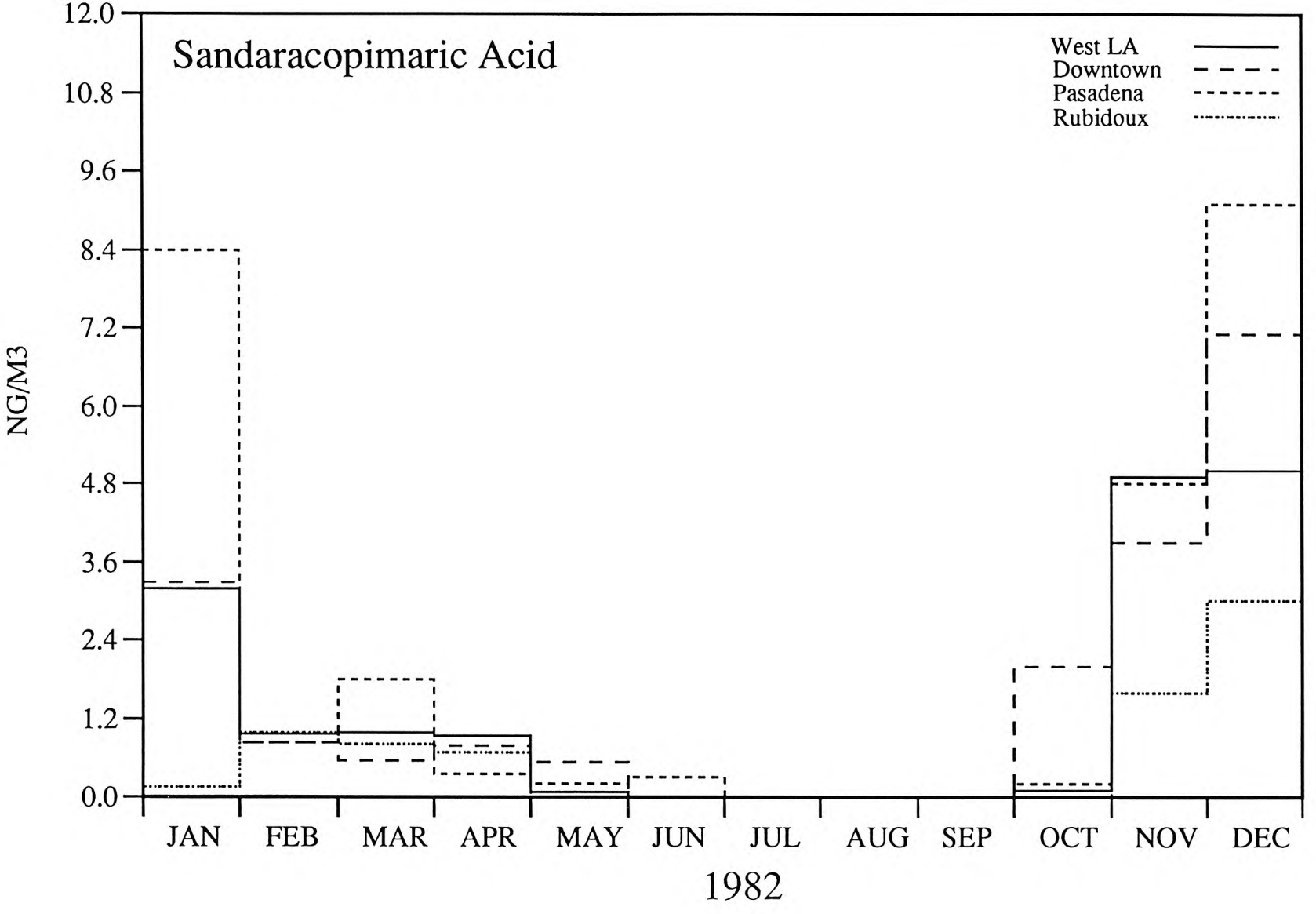

13-Isopropyl-5alpha-podocarpa-6,8,11,13-tetraen-16-oic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
7.0
6.3
5.6
4.9
4.2
3.5
2.8
2.1
1.4
0.7
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

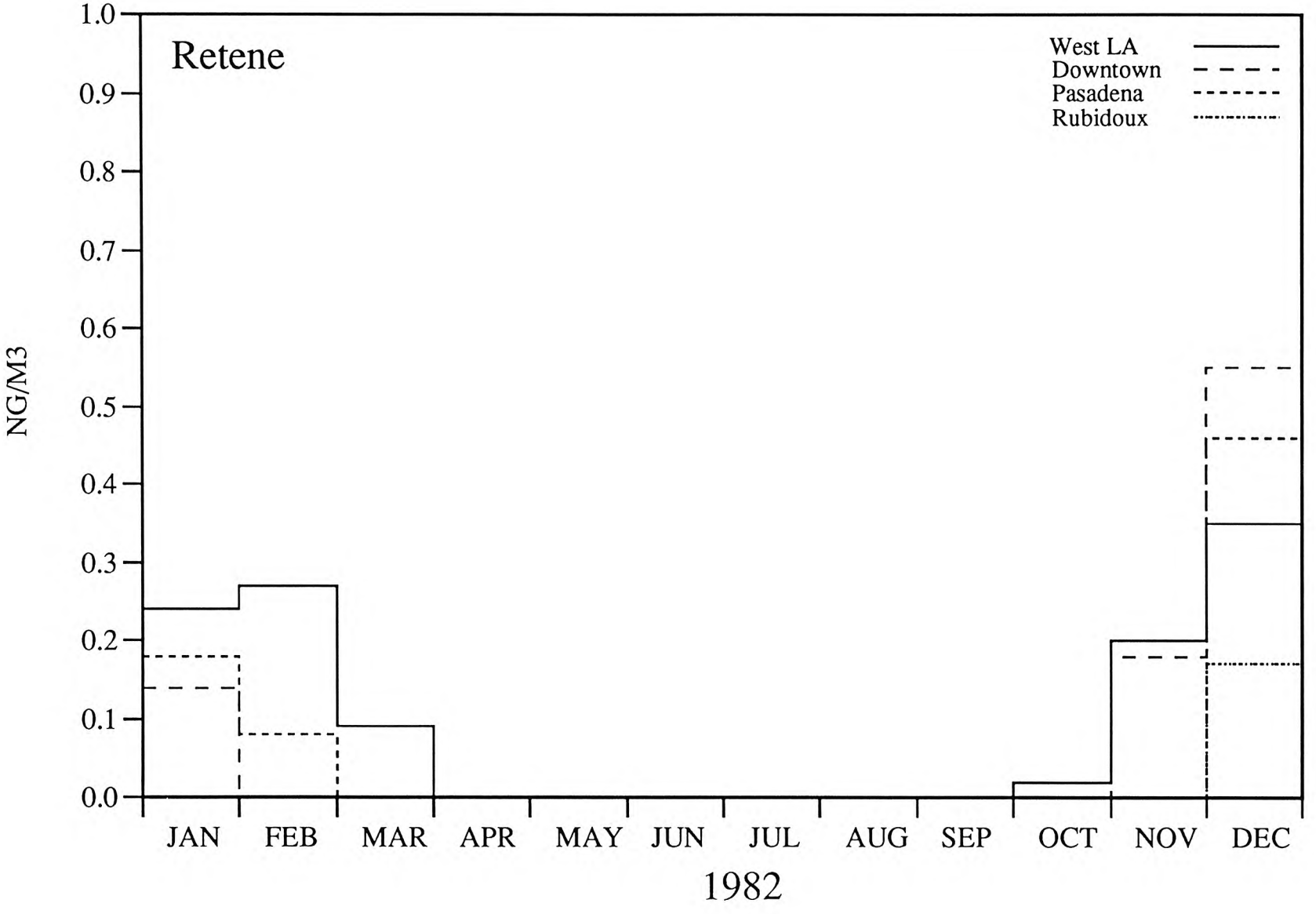

8,15-Pimaradien-18-oic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
7.0
6.3
5.6
4.9
4.2
3.5
2.8
2.1
1.4
0.7
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Pimaric Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
25.0
22.5
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Isopimaric Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
14.0
12.6
11.2
9.8
8.4
7.0
5.6
4.2
2.8
1.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

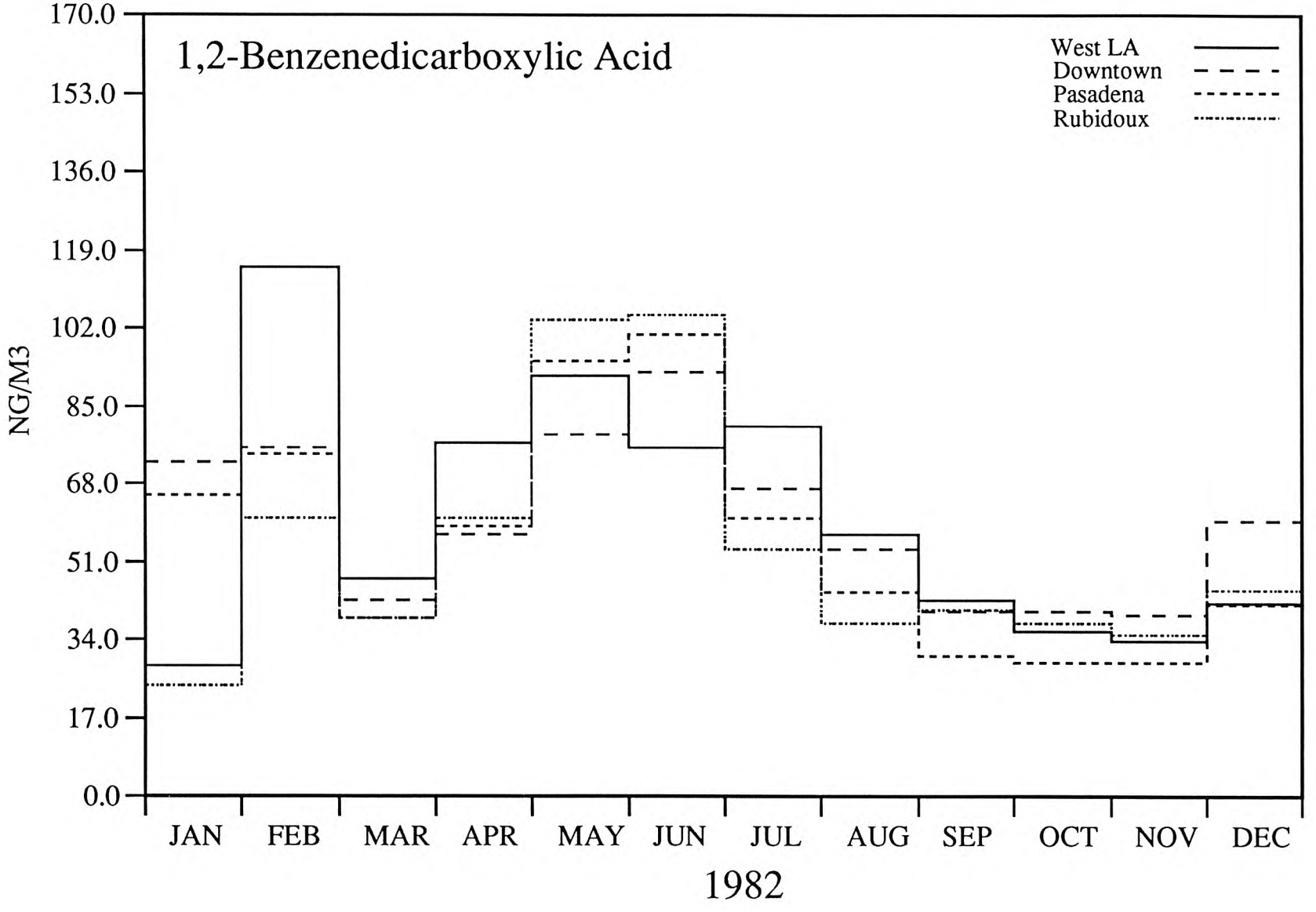

7-Oxodehydroabietic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
19.0
17.1
15.2
13.3
11.4
9.5
7.6
5.7
3.8
1.9
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

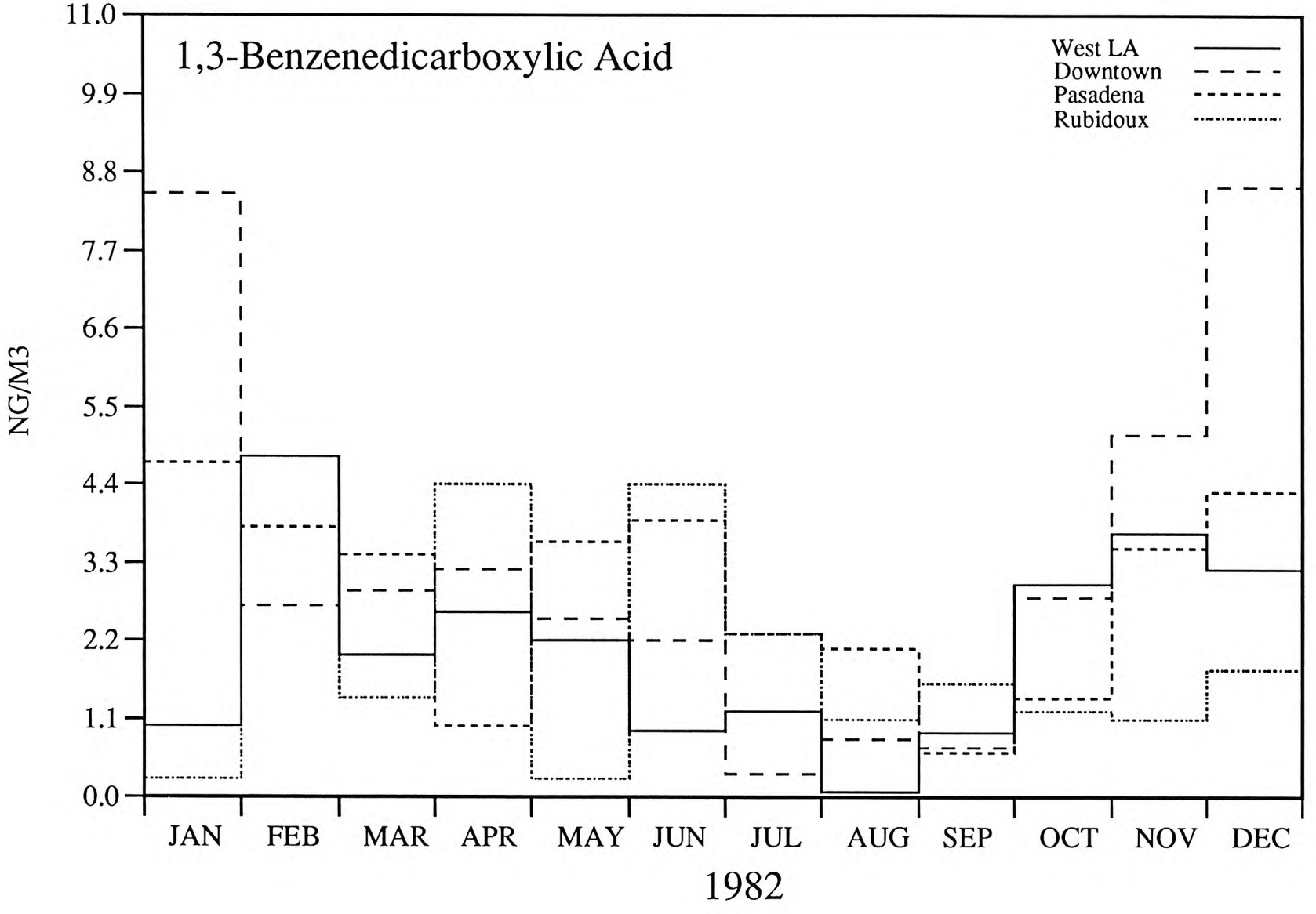

Sandaracopimaric Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
12.0
10.8
9.6
8.4
7.2
6.0
4.8
3.6
2.4
1.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

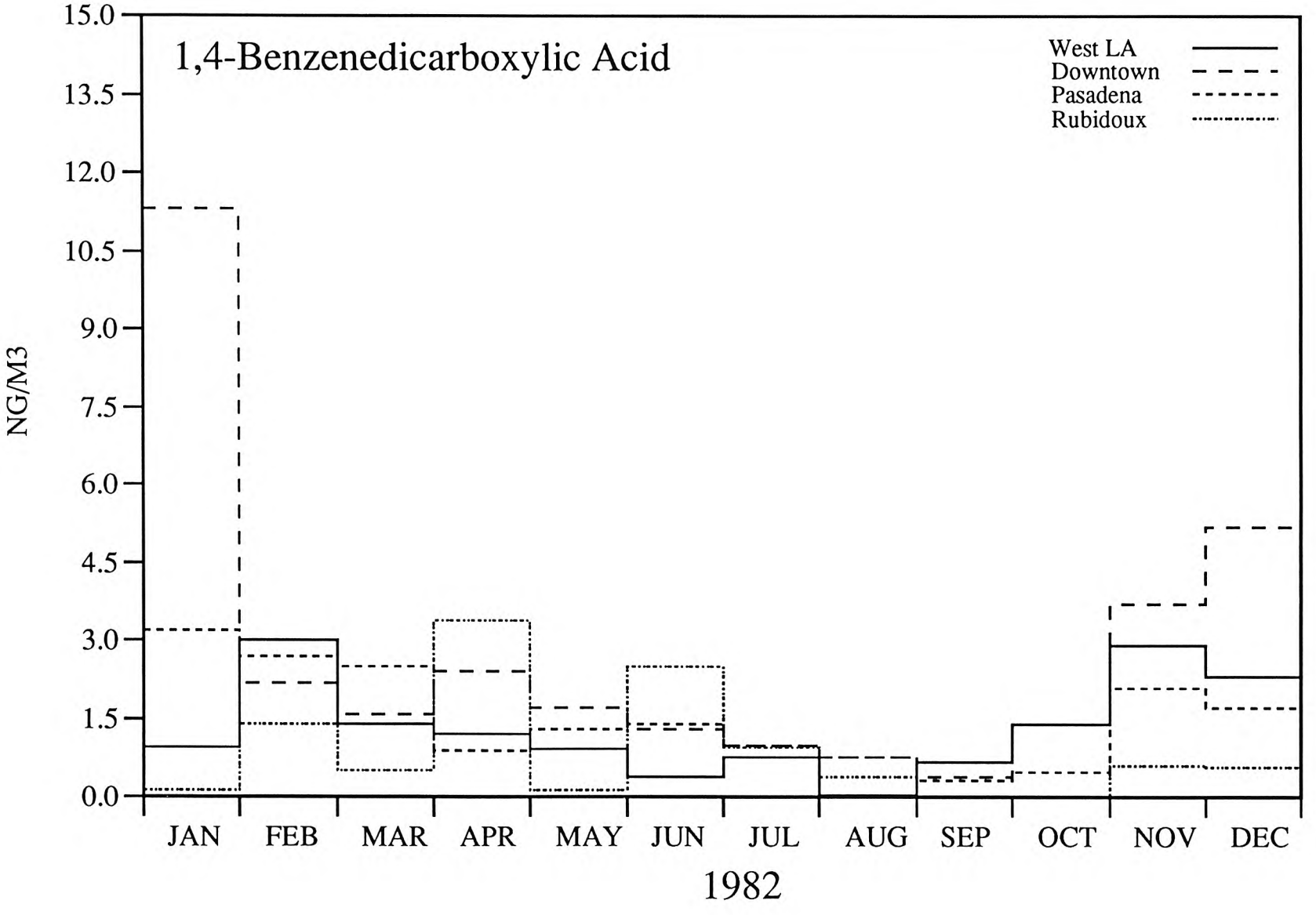

Retene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

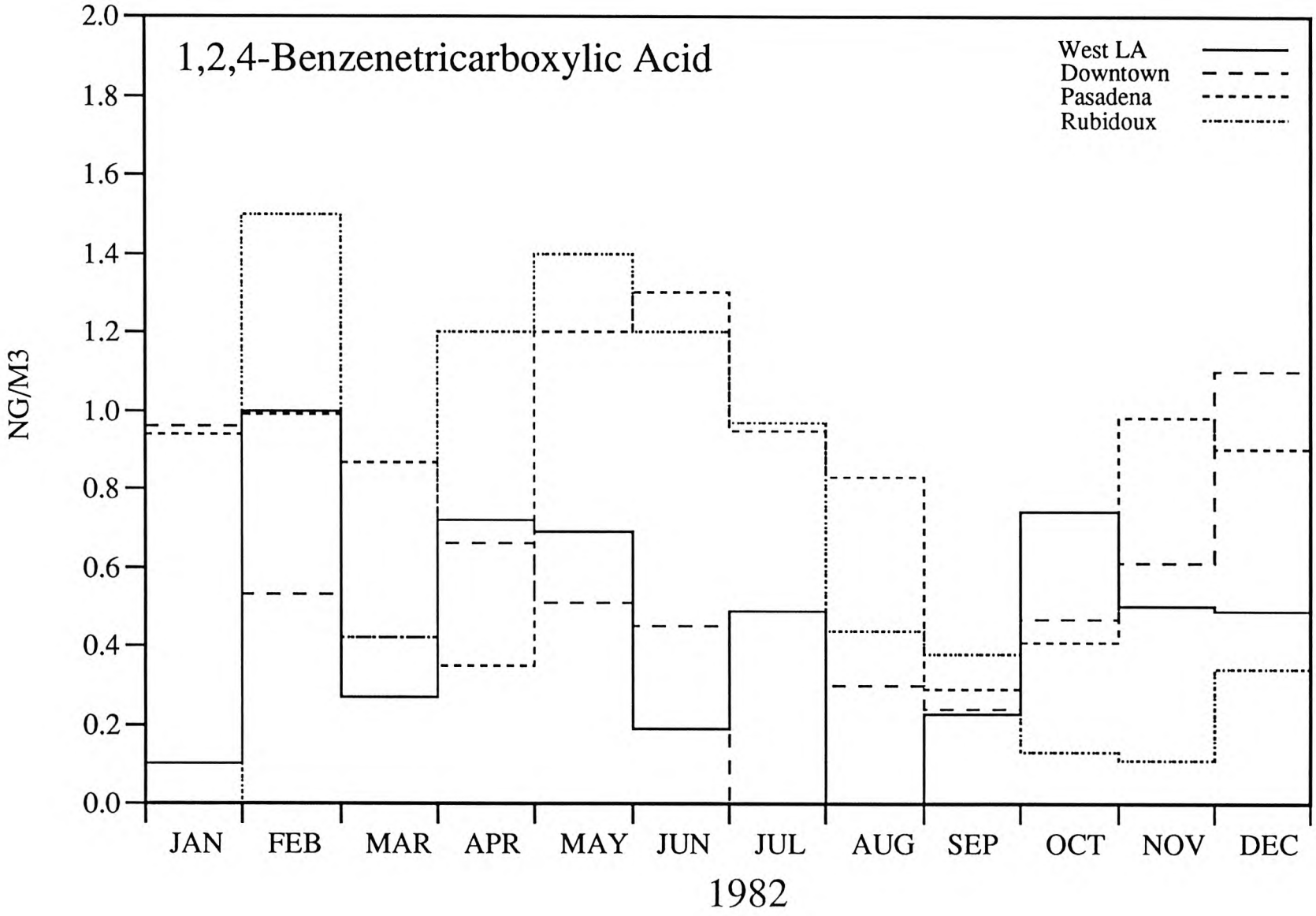
Appendix A7

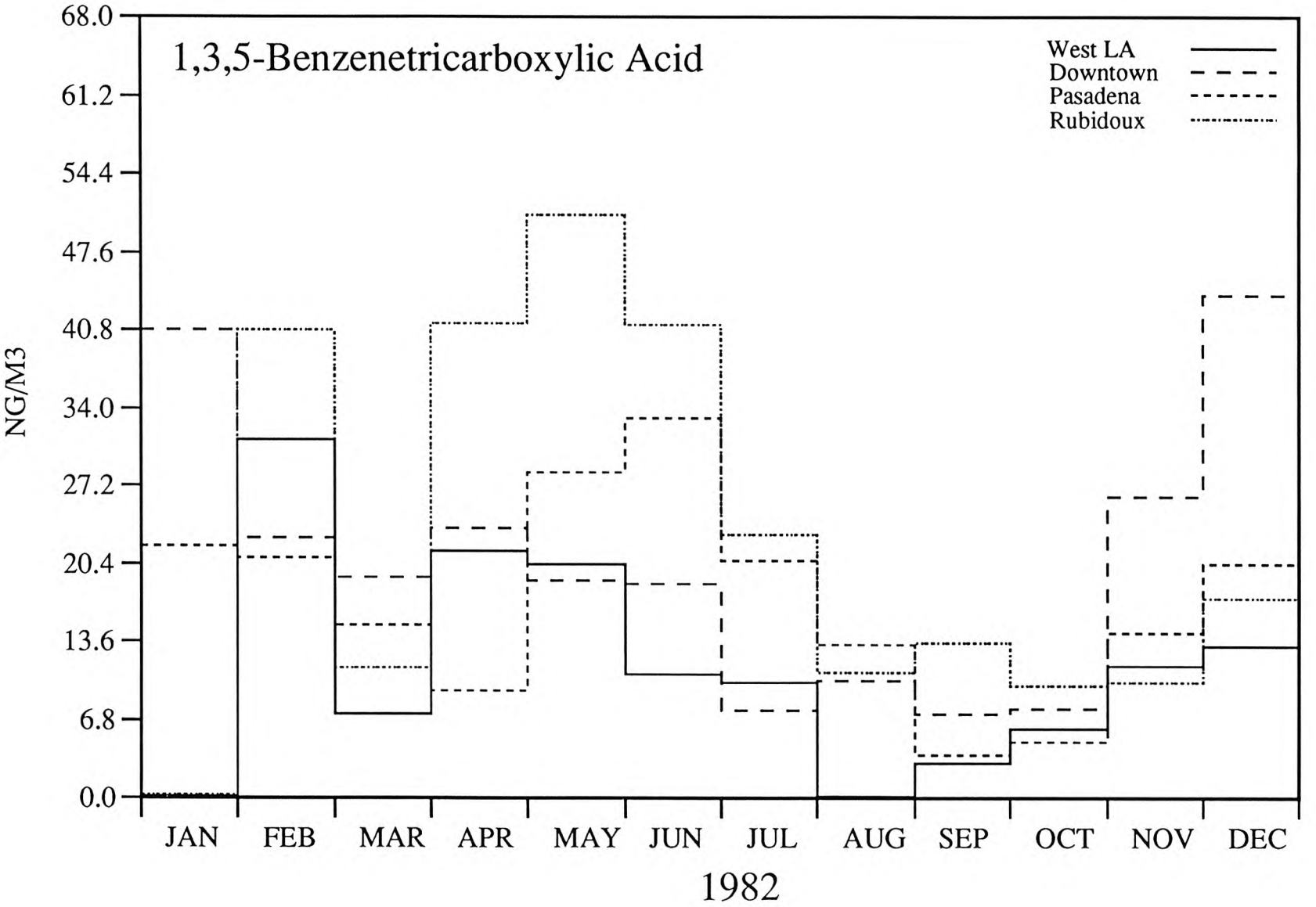
Ambient Concentration Profiles for Aromatic Polycarboxylic Acids

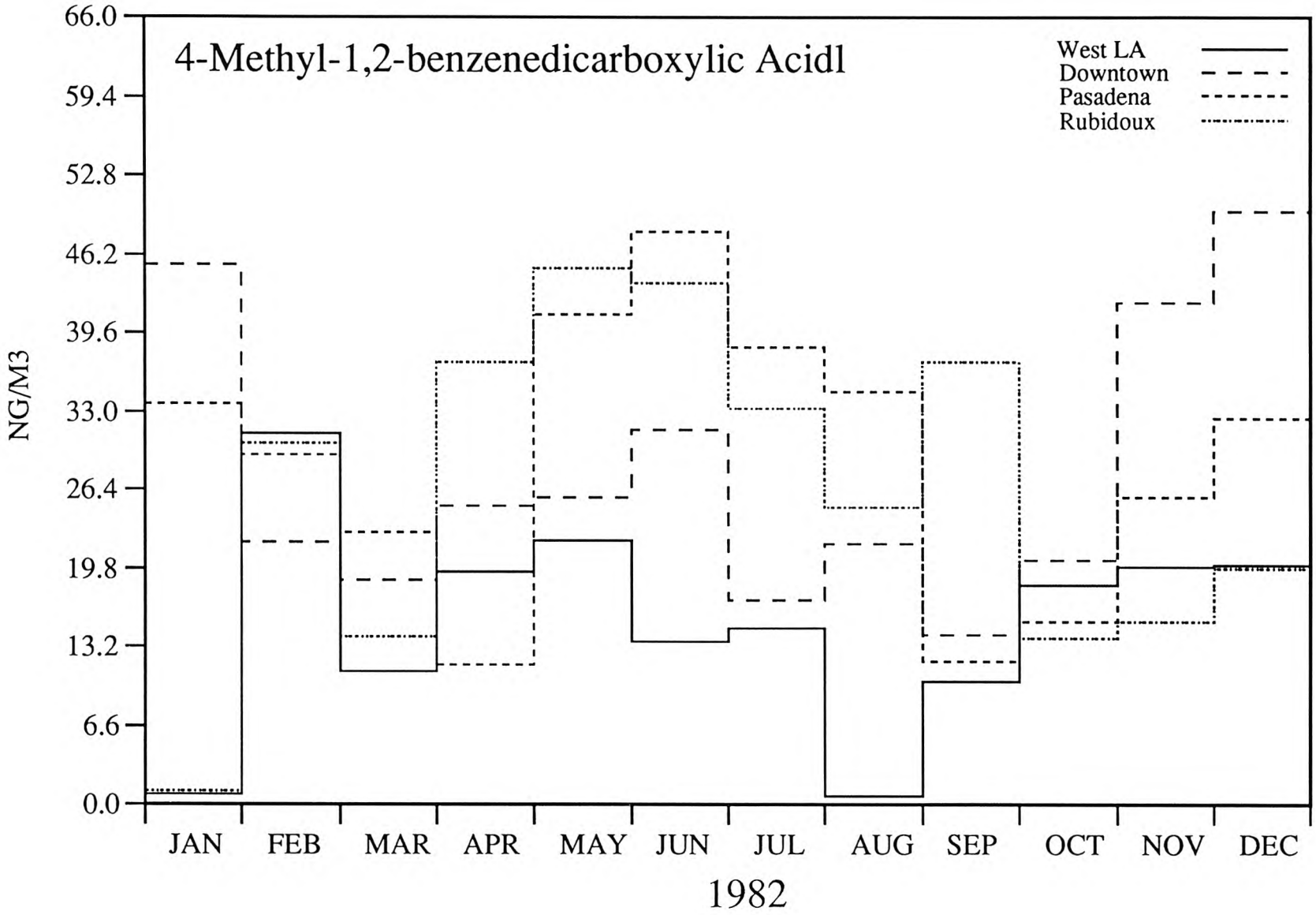

1,2-Benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
170.0
153.0
136.0
119.0
102.0
85.0
68.0
51.0
34.0
17.0
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

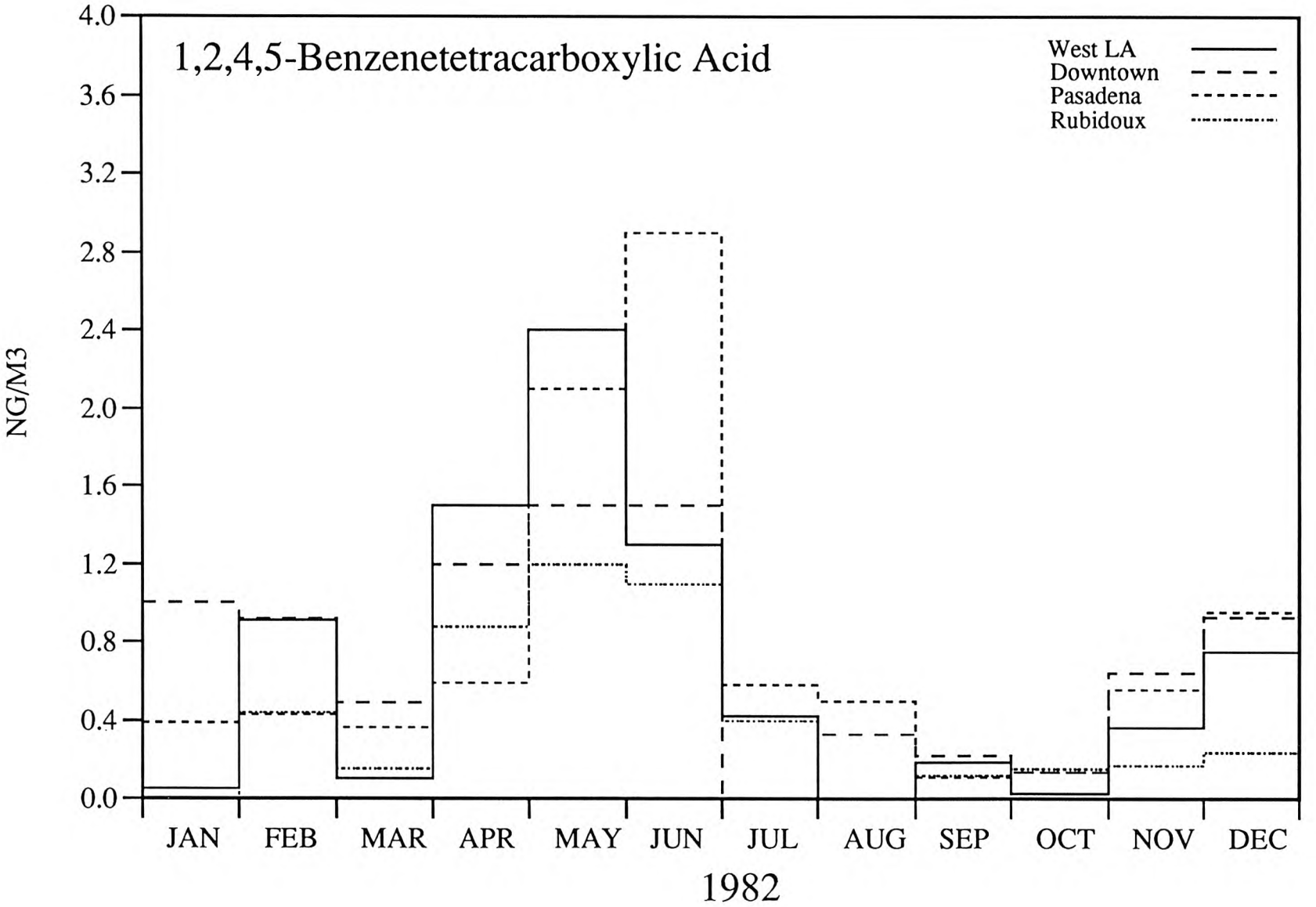

1,3-Benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
11.0
9.9
8.8
7.7
6.6
5.5
4.4
3.3
2.2
1.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


1,4-Benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
15.0
13.5
12.0
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


1,2,4-Benzenetricarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

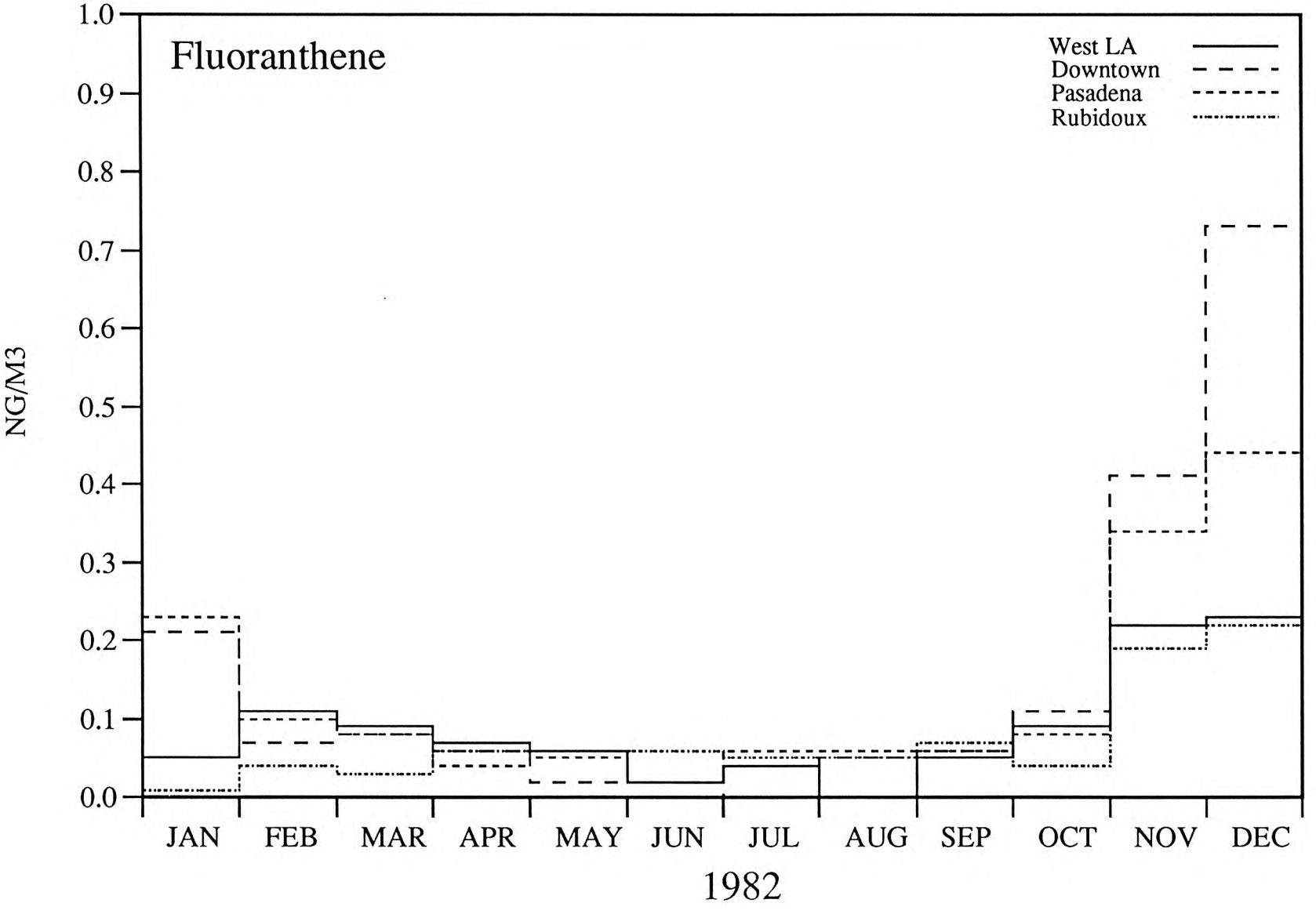

1,3,5-Benzenetricarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
68.0
61.2
54.4
47.6
40.8
34.0
27.2
20.4
13.6
6.8
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

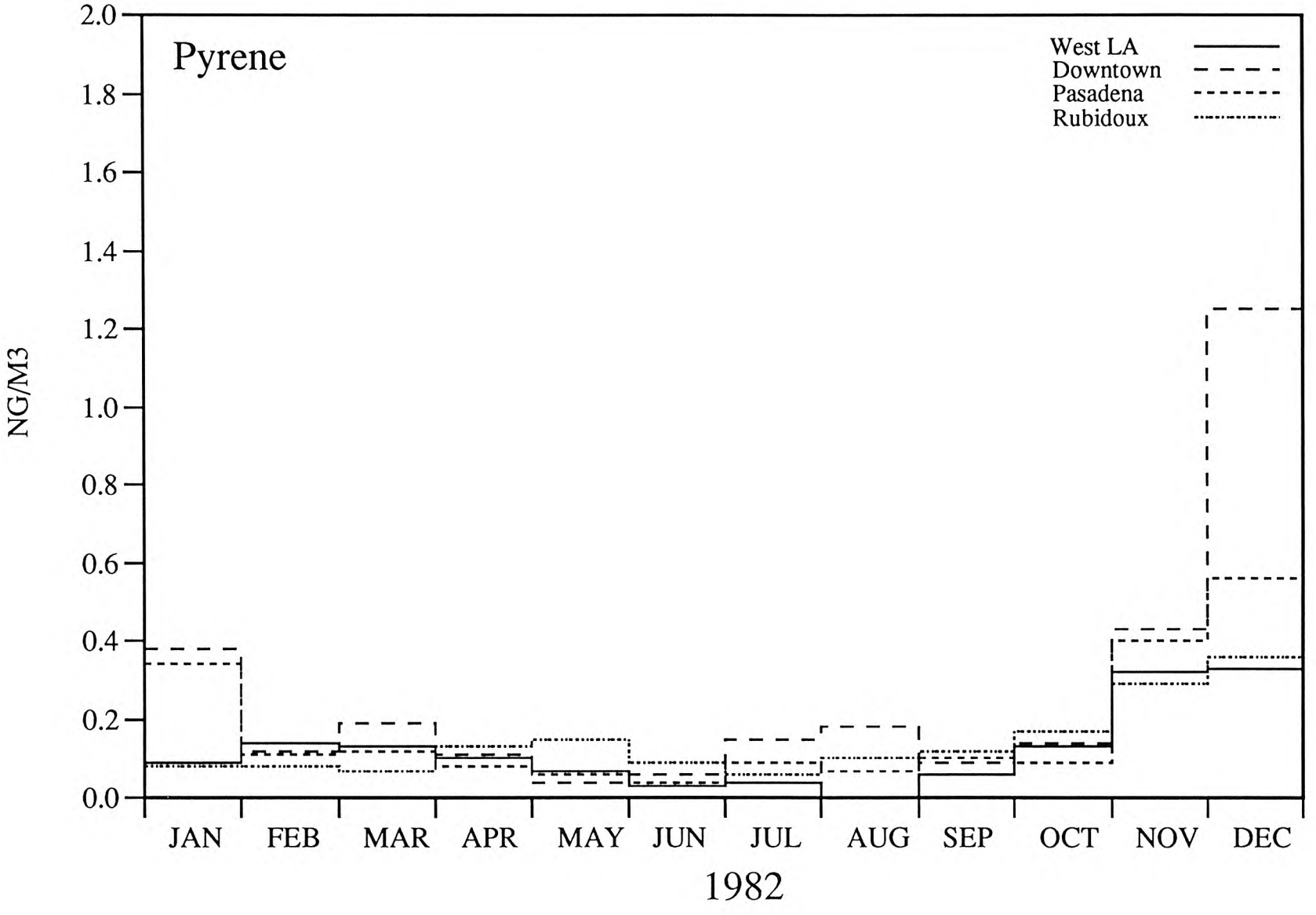

4-Methyl-1,2-benzenedicarboxylic Acidl
West LA
Downtown
Pasadena
Rubidoux
NG/M3
66.0
59.4
52.8
46.2
39.6
33.0
26.4
19.8
13.2
6.6
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

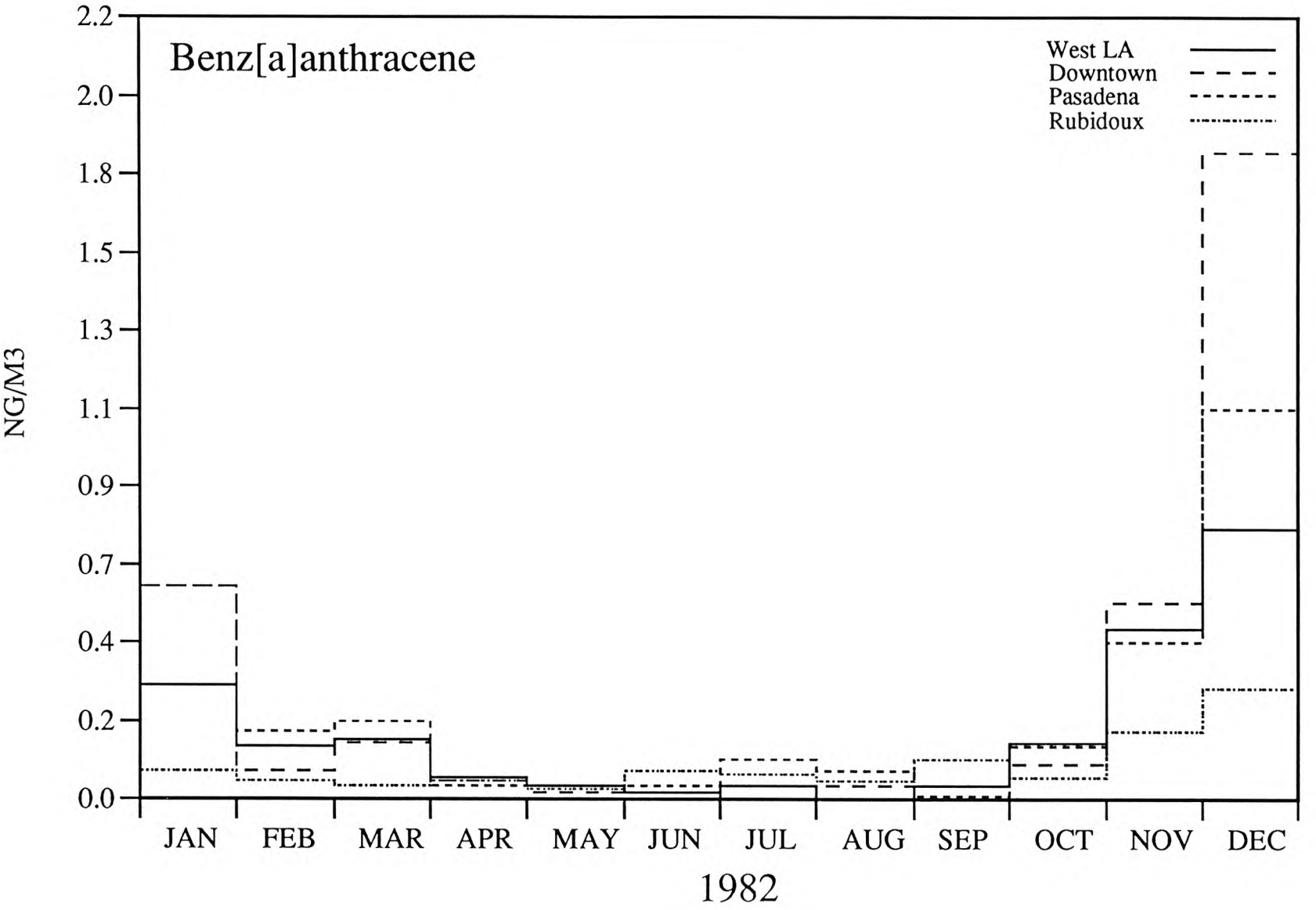

1,2,4,5-Benzenetetracarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
NG/M3
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

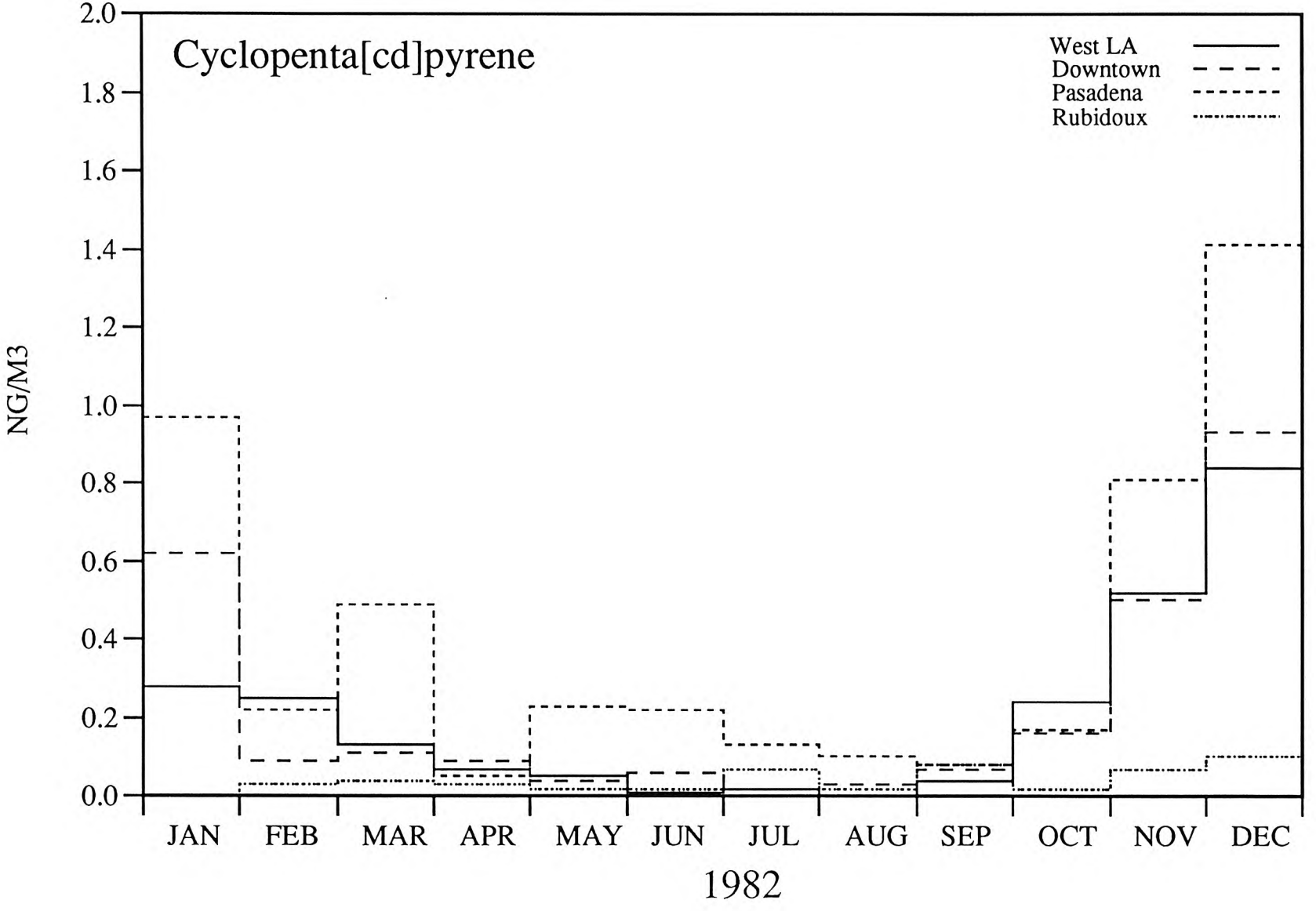
Appendix A8

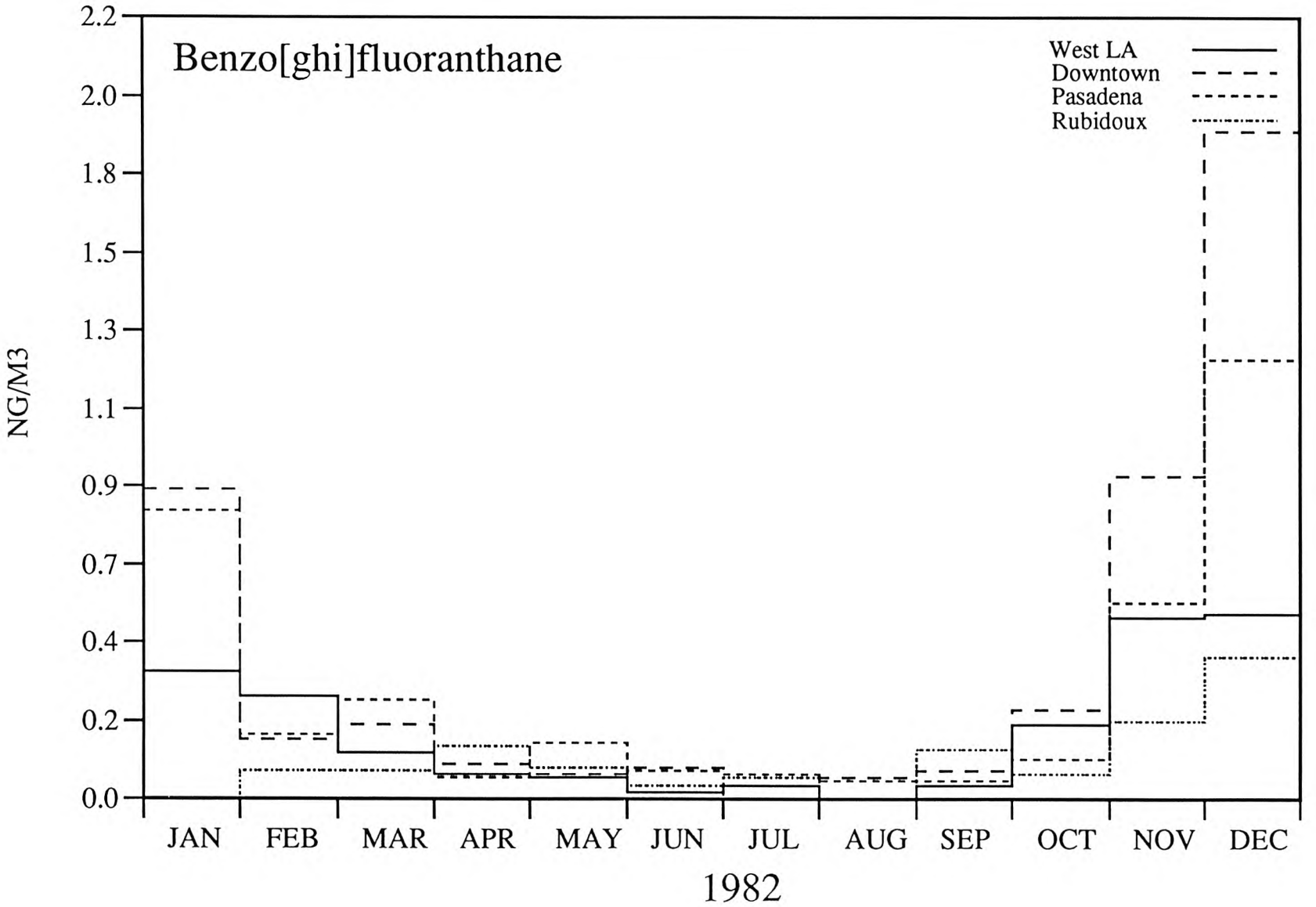
Ambient Concentration Profiles for Polycyclic Aromatic Hydrocarbons PAH's

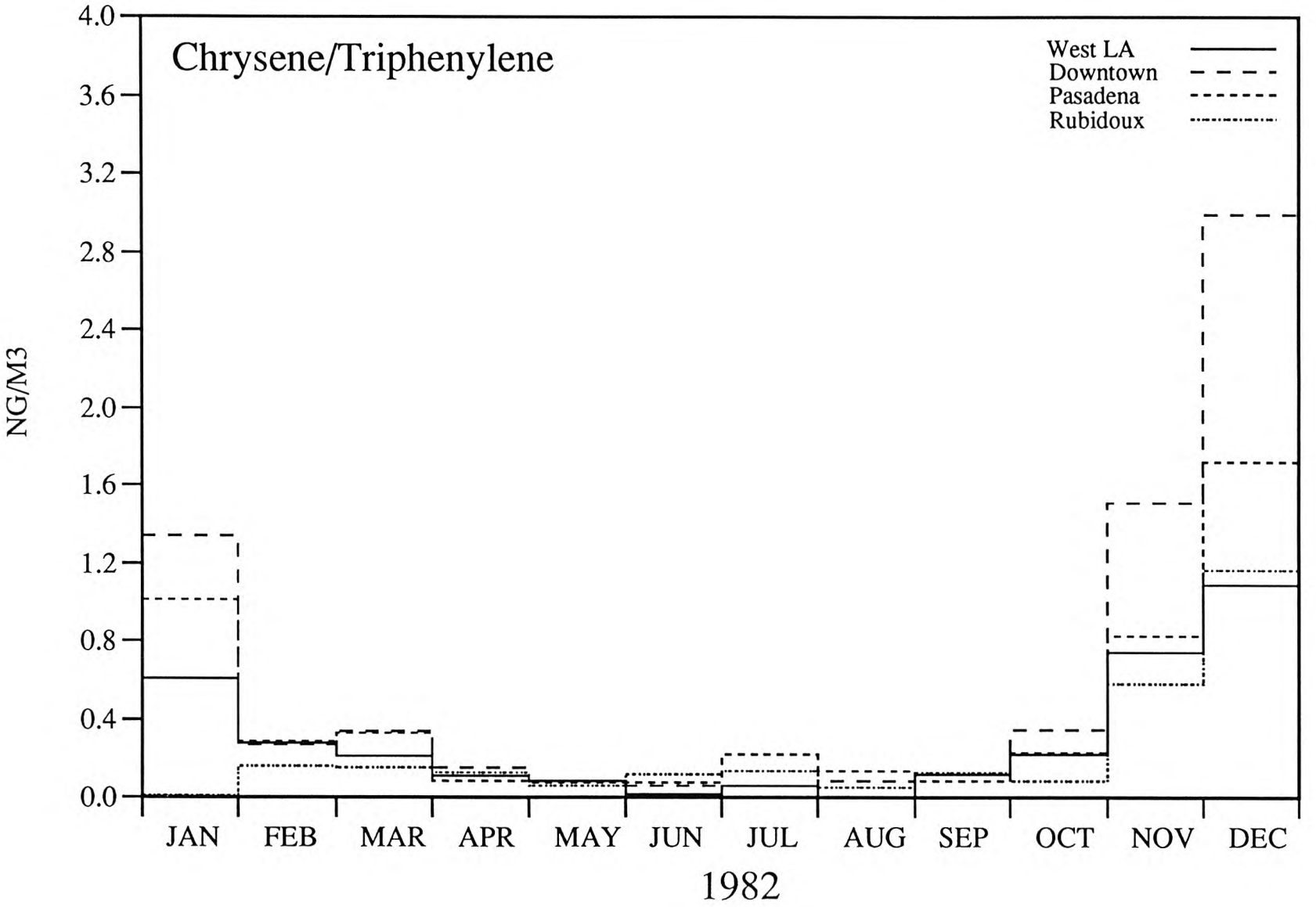

Fluoranthene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

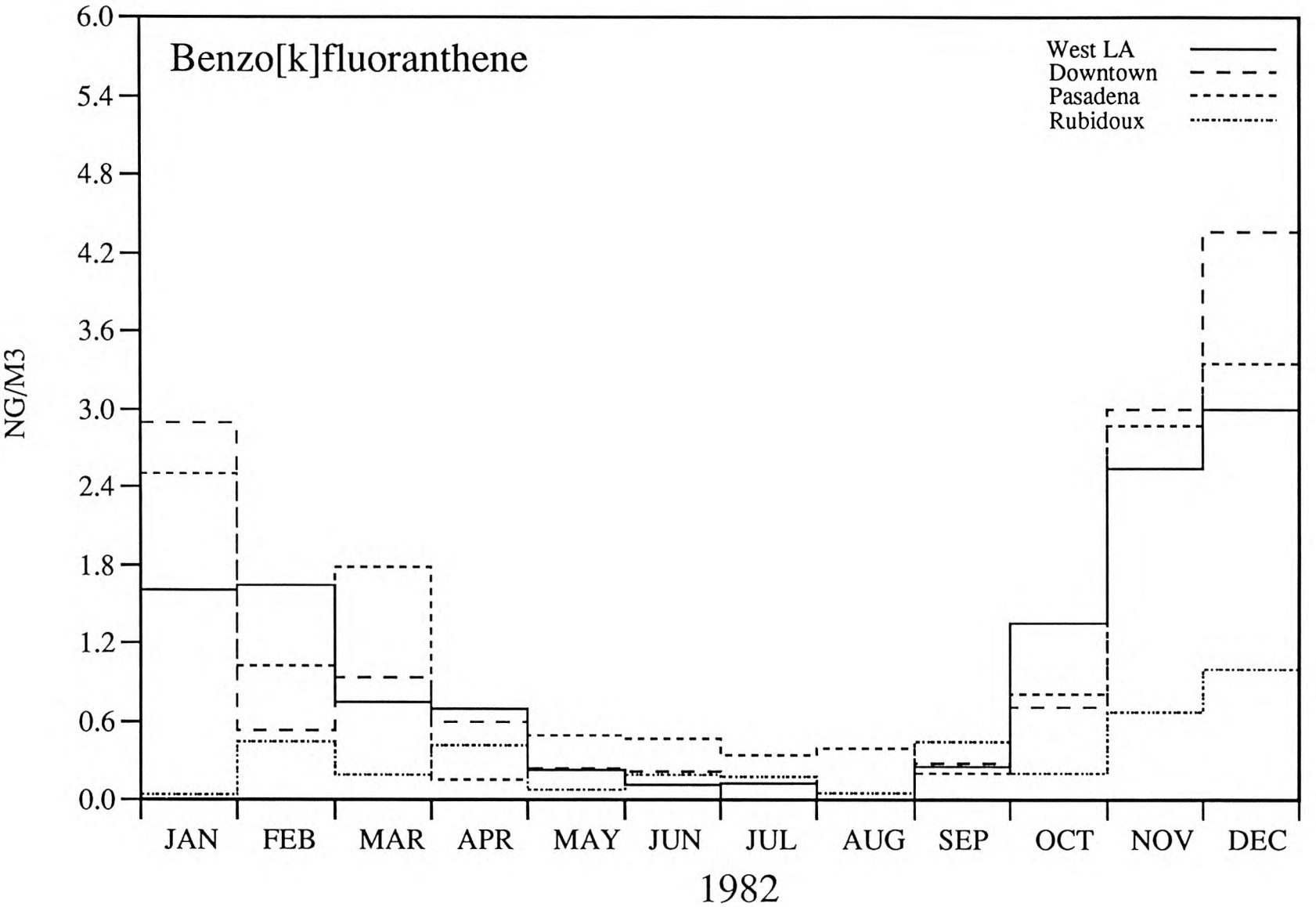

Pyrene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

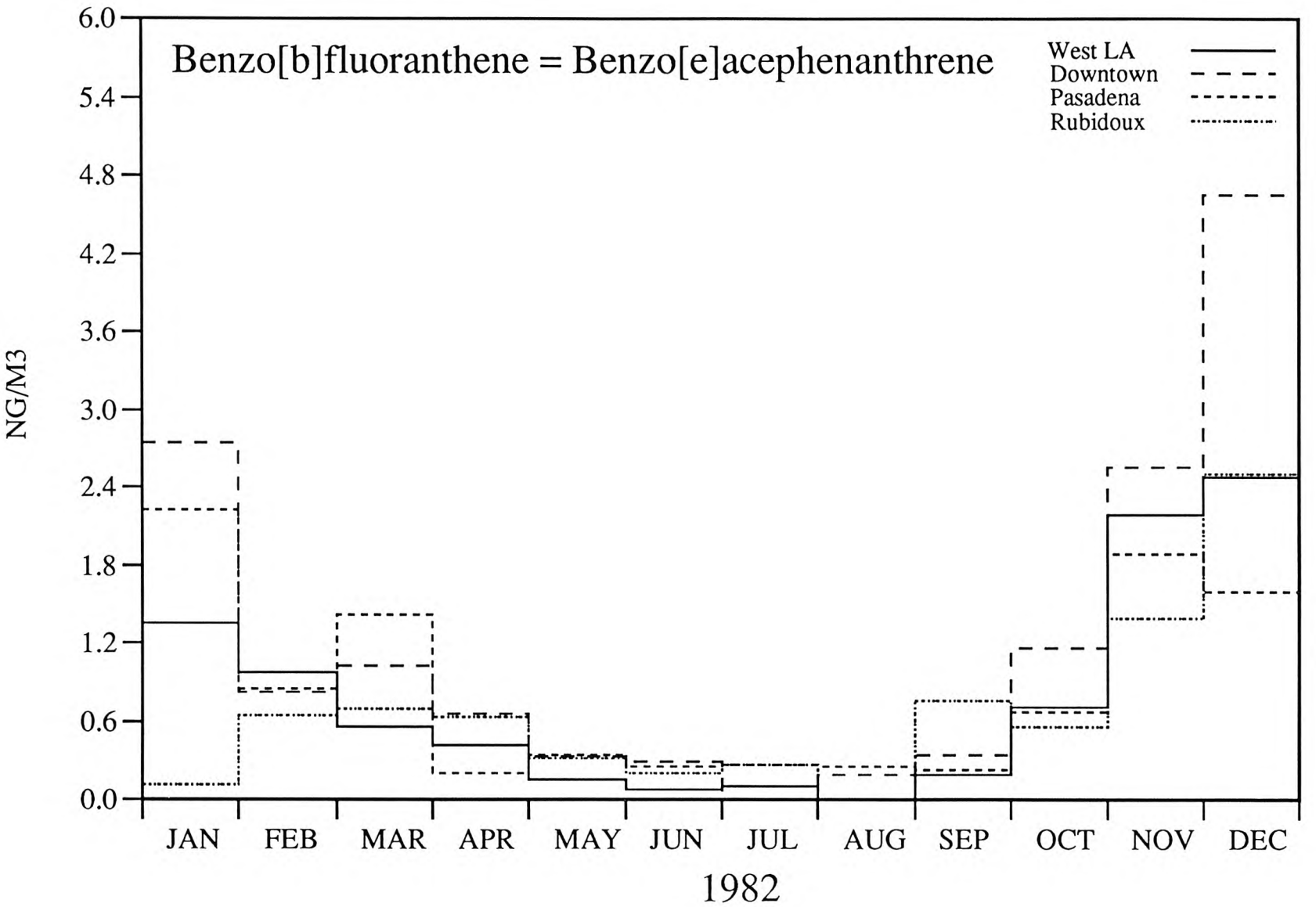

Benz[a]anthracene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.2
2.0
1.8
1.5
1.3
1.1
0.9
0.7
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

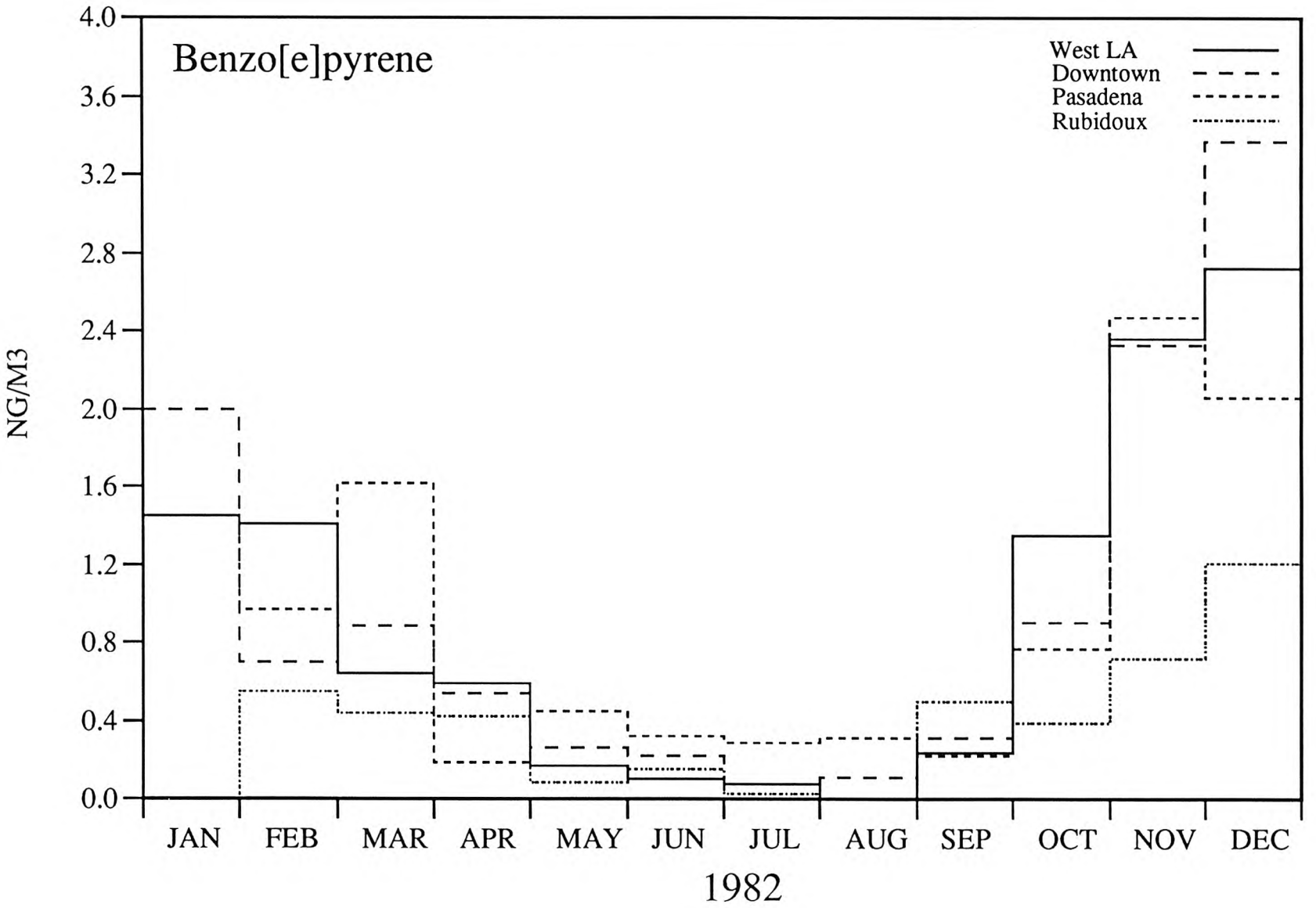

Cyclopenta[cd]pyrene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

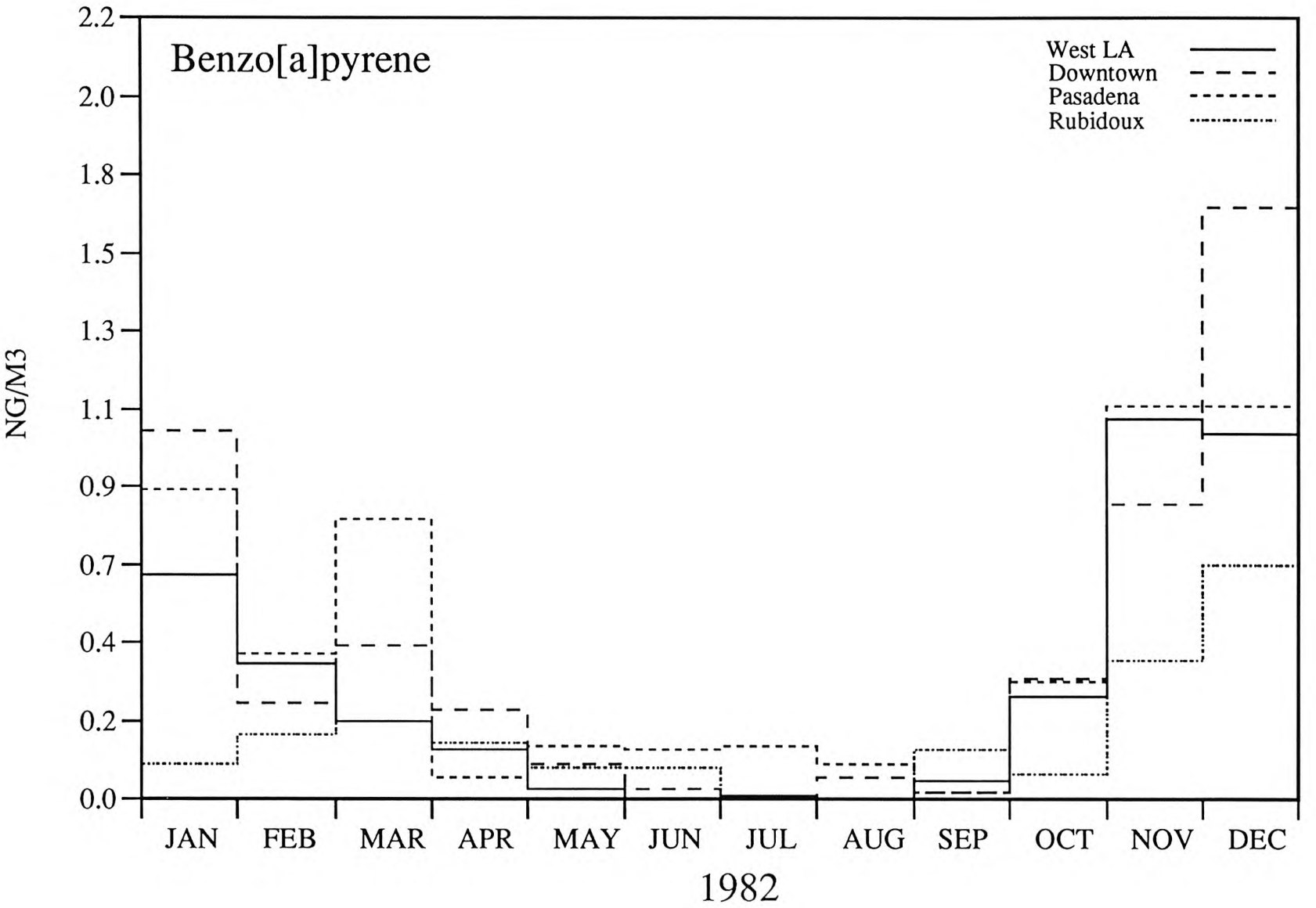

Benzo[ghi]fluoranthane
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.2
2.0
1.8
1.5
1.3
1.1
0.9
0.7
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

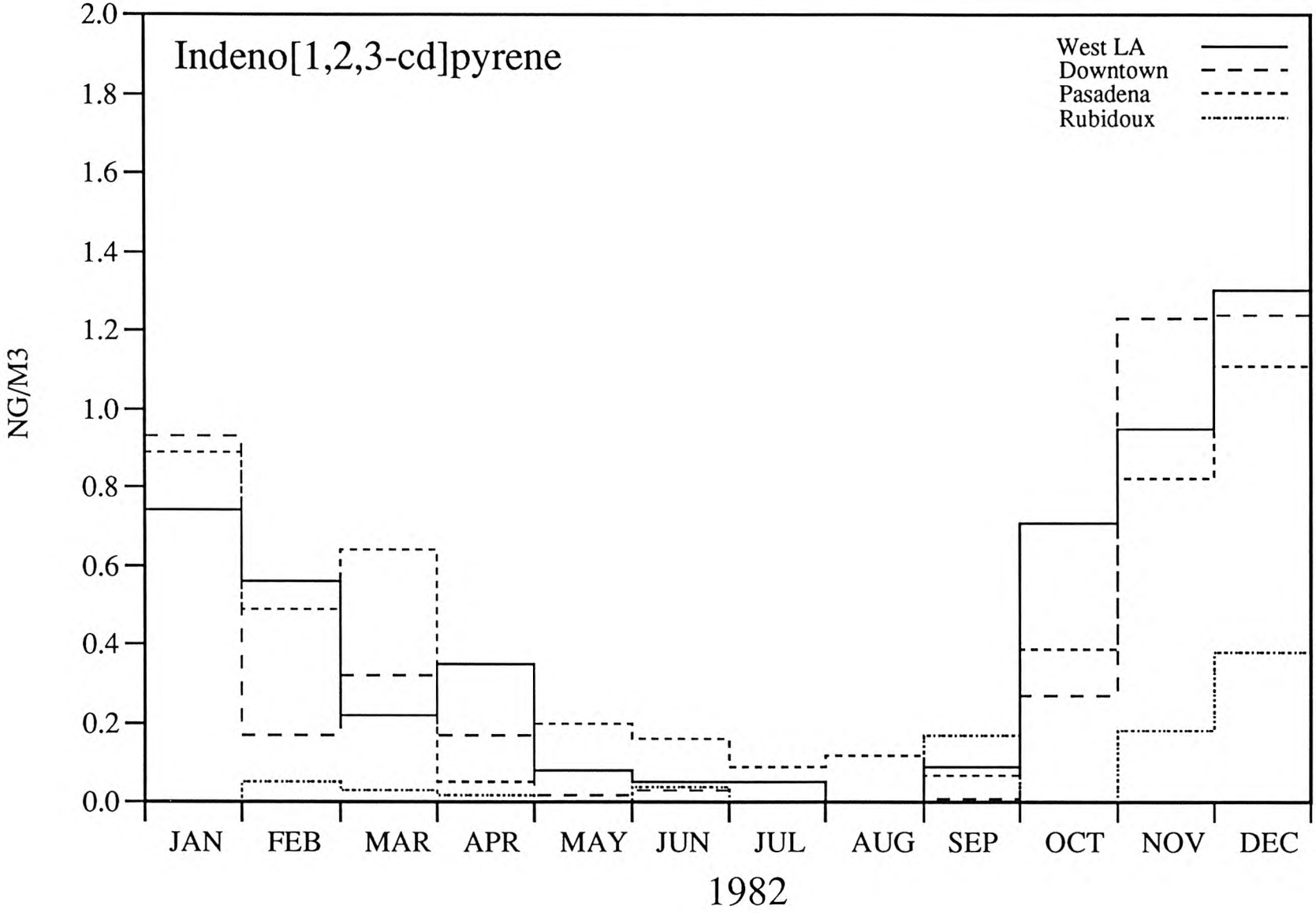

Chrysene/Triphenylene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

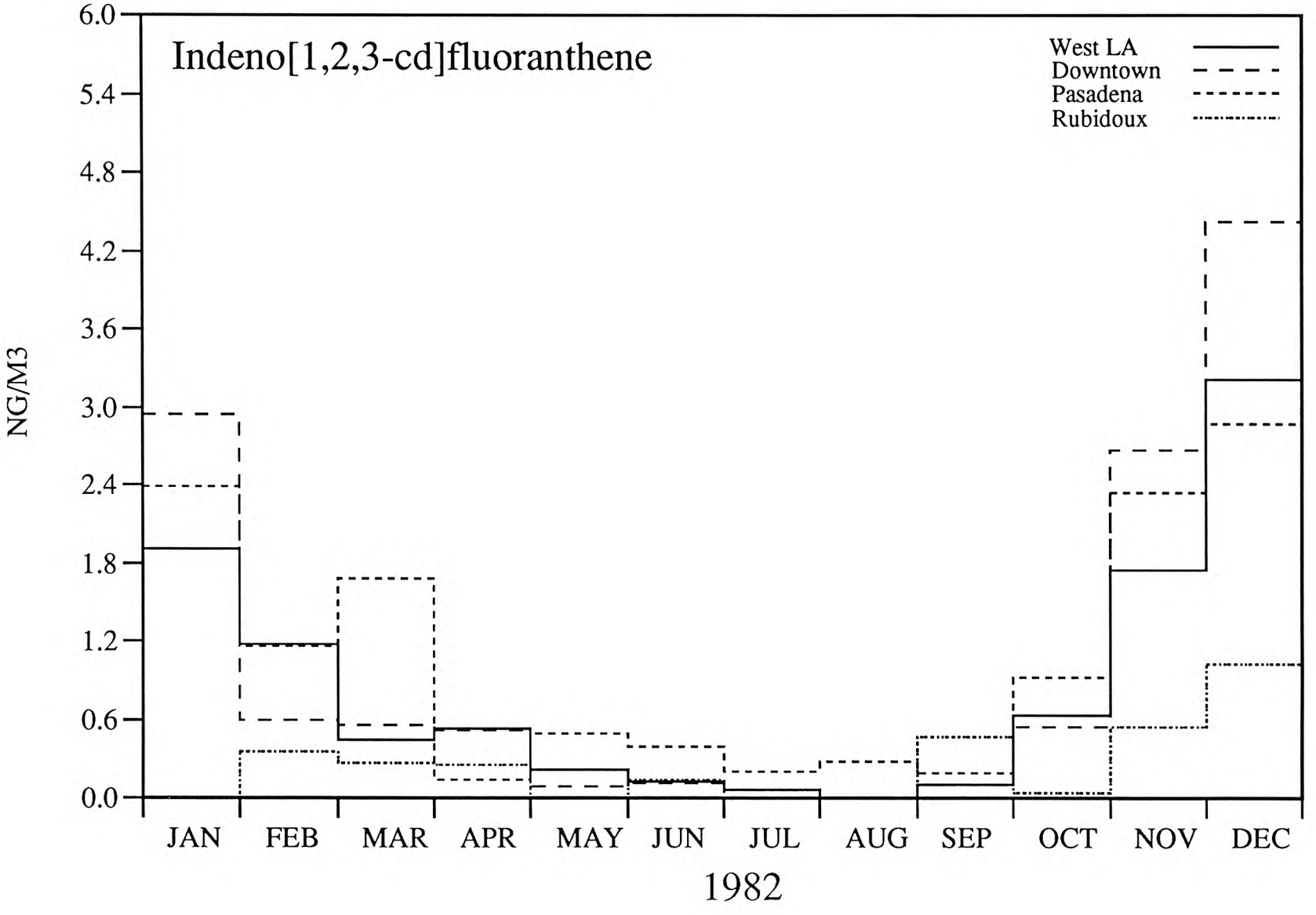

Benzo[k]fluoranthene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
0.6
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

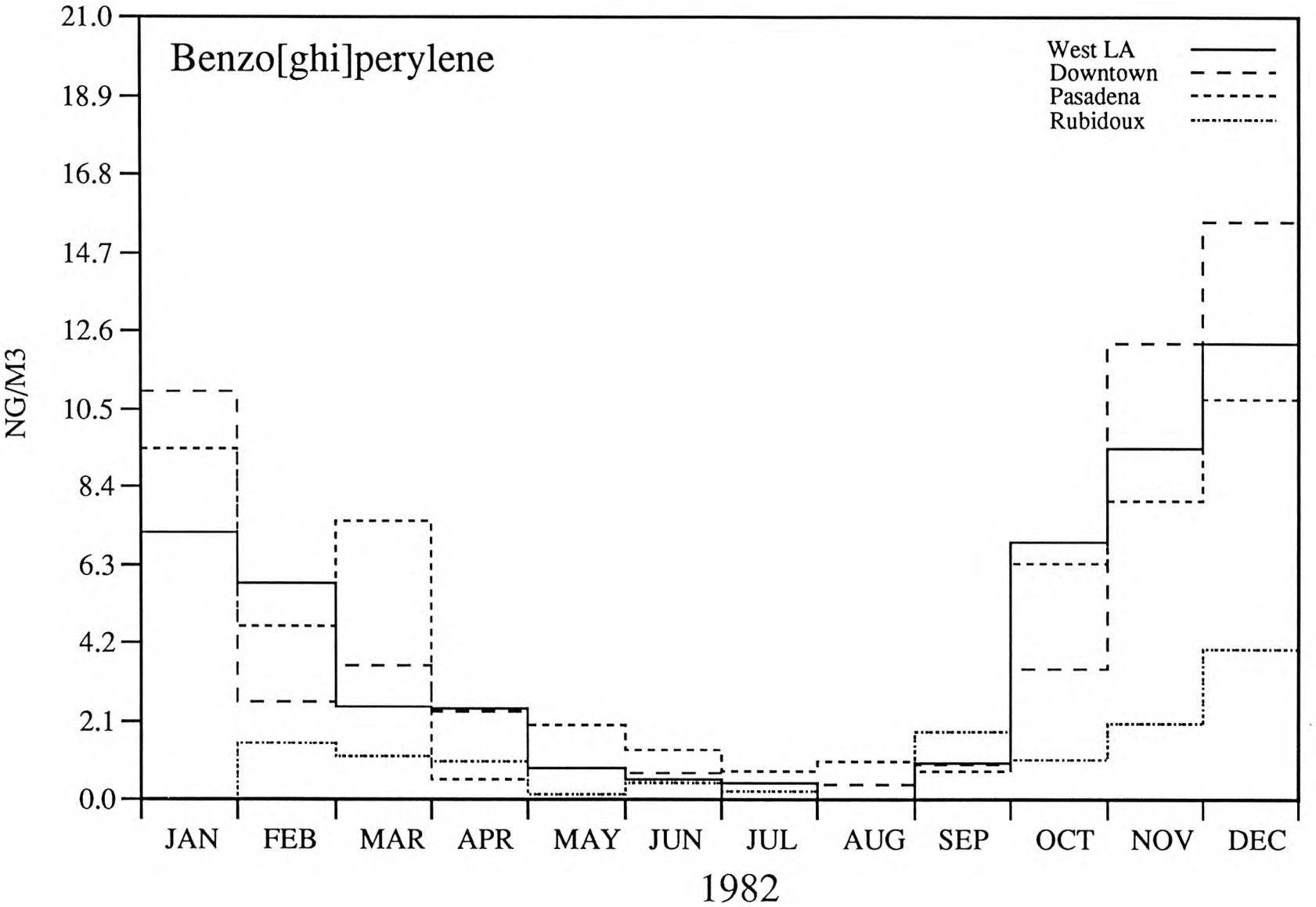

Benzo[b]fluoranthene = Benzo[e]acephenanthrene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
0.6
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

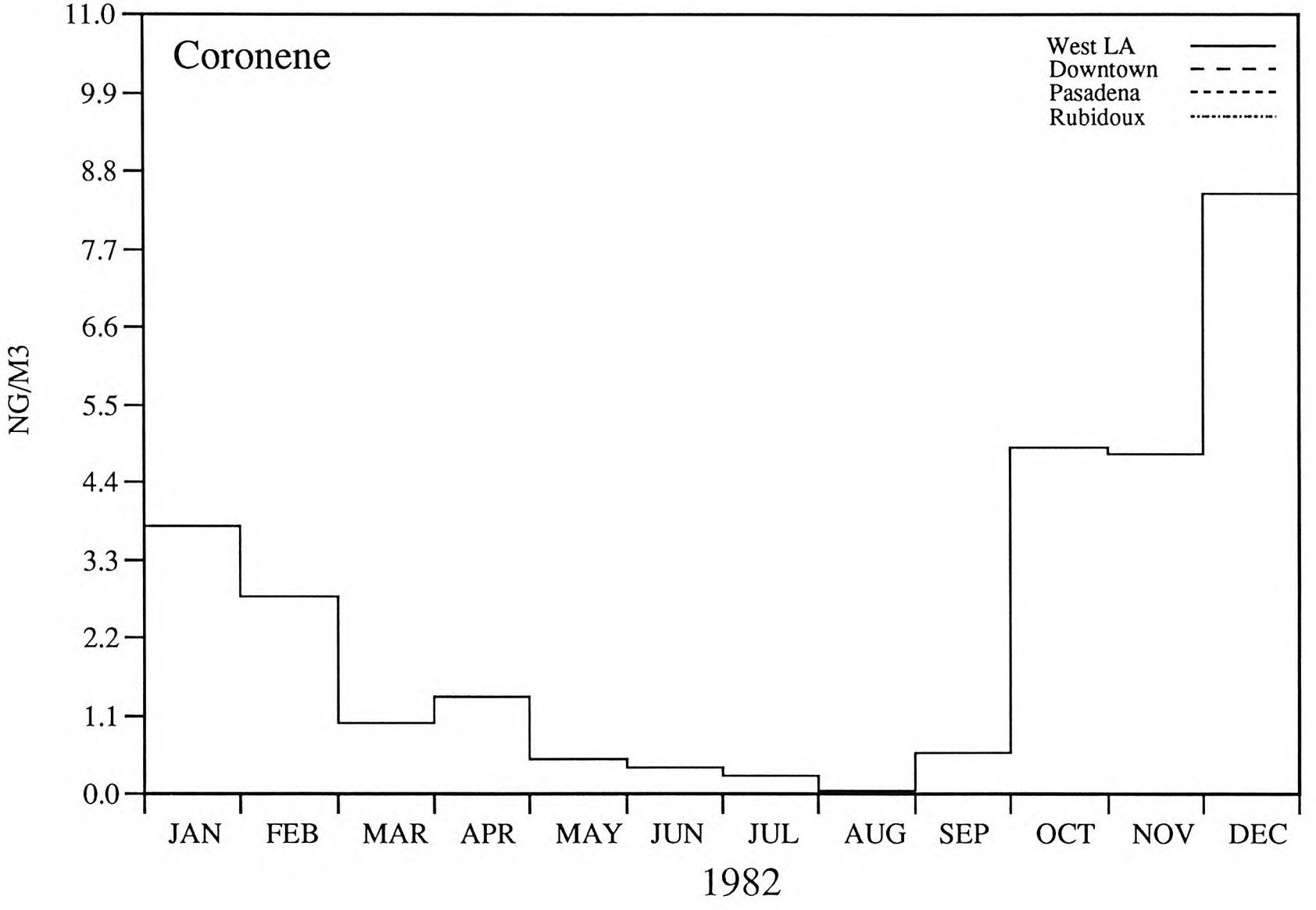

Benzo[e]pyrene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Benzo[a]pyrene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.2
2.0
1.8
1.5
1.3
1.1
0.9
0.7
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Indeno[1,2,3-cd]pyrene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

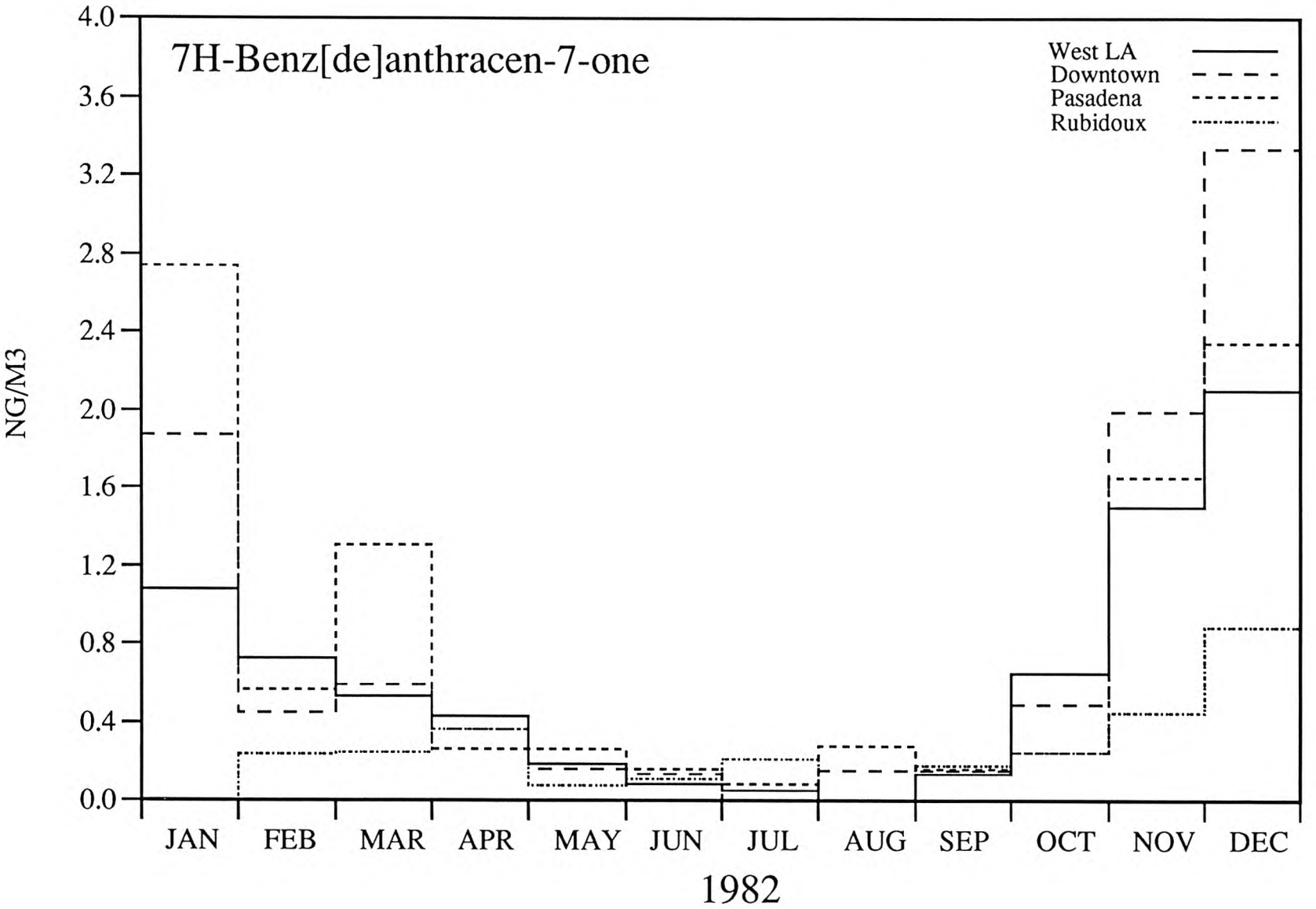

Indeno[1,2,3-cd]fluoranthene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
0.6
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

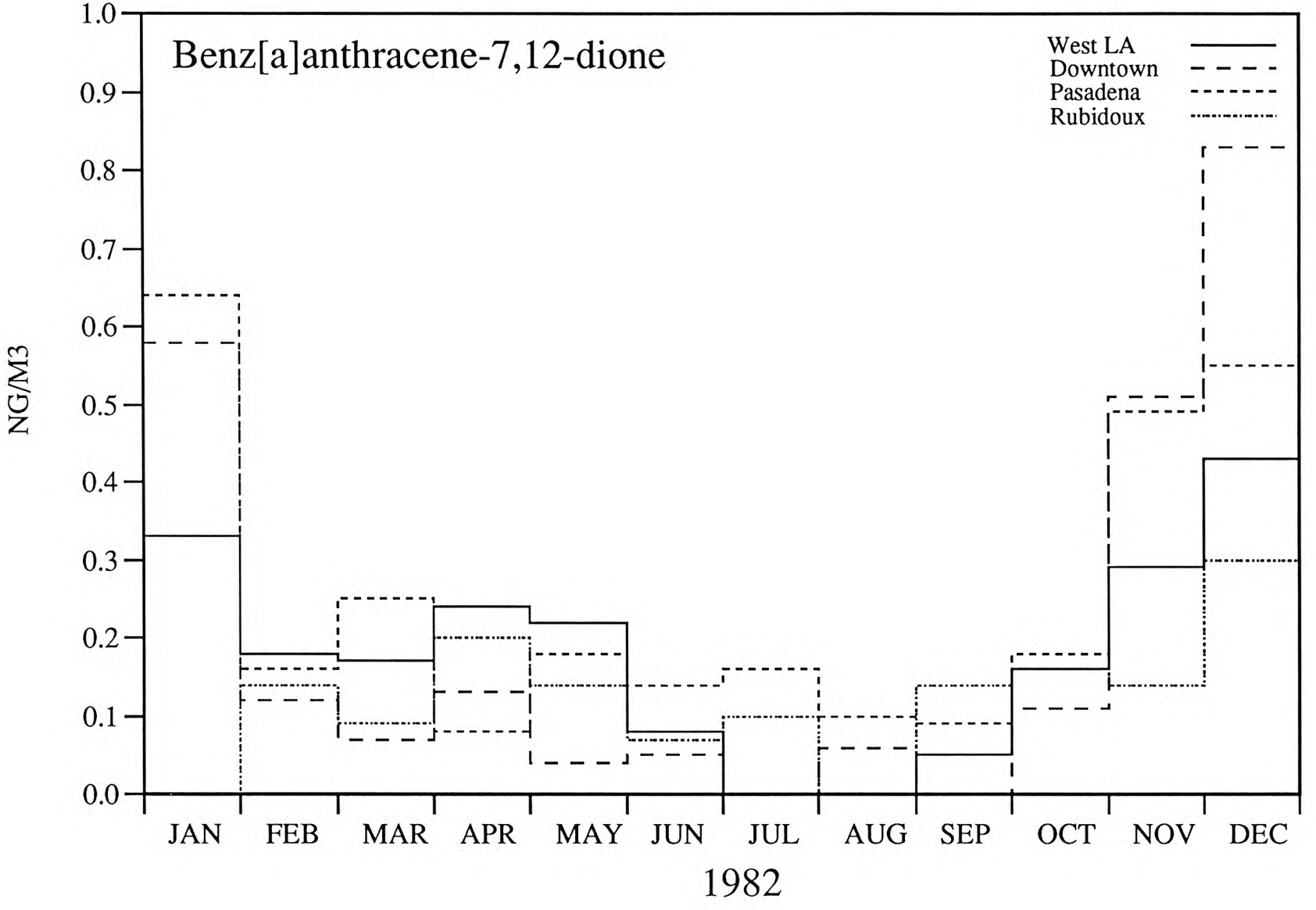

Benzo[ghi]perylene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
21.0
18.9
16.8
14.7
12.6
10.5
8.4
6.3
4.2
2.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

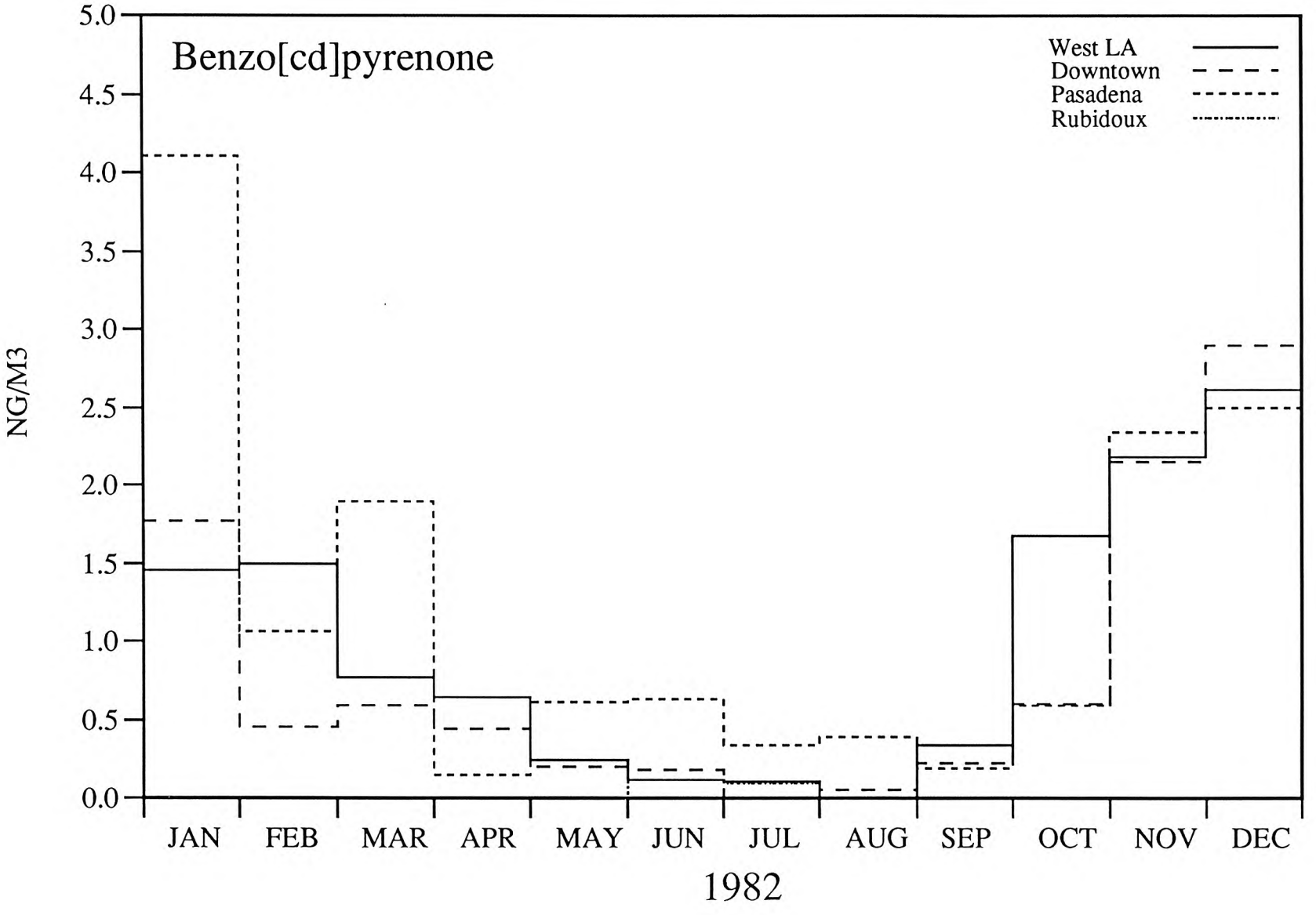

Coronene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
11.0
9.9
8.8
7.7
6.6
5.5
4.4
3.3
2.2
1.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

Appendix A9

Ambient Concentration Profiles for Polycyclic Aromatic Ketones and Quinones PAK's + PAQ's

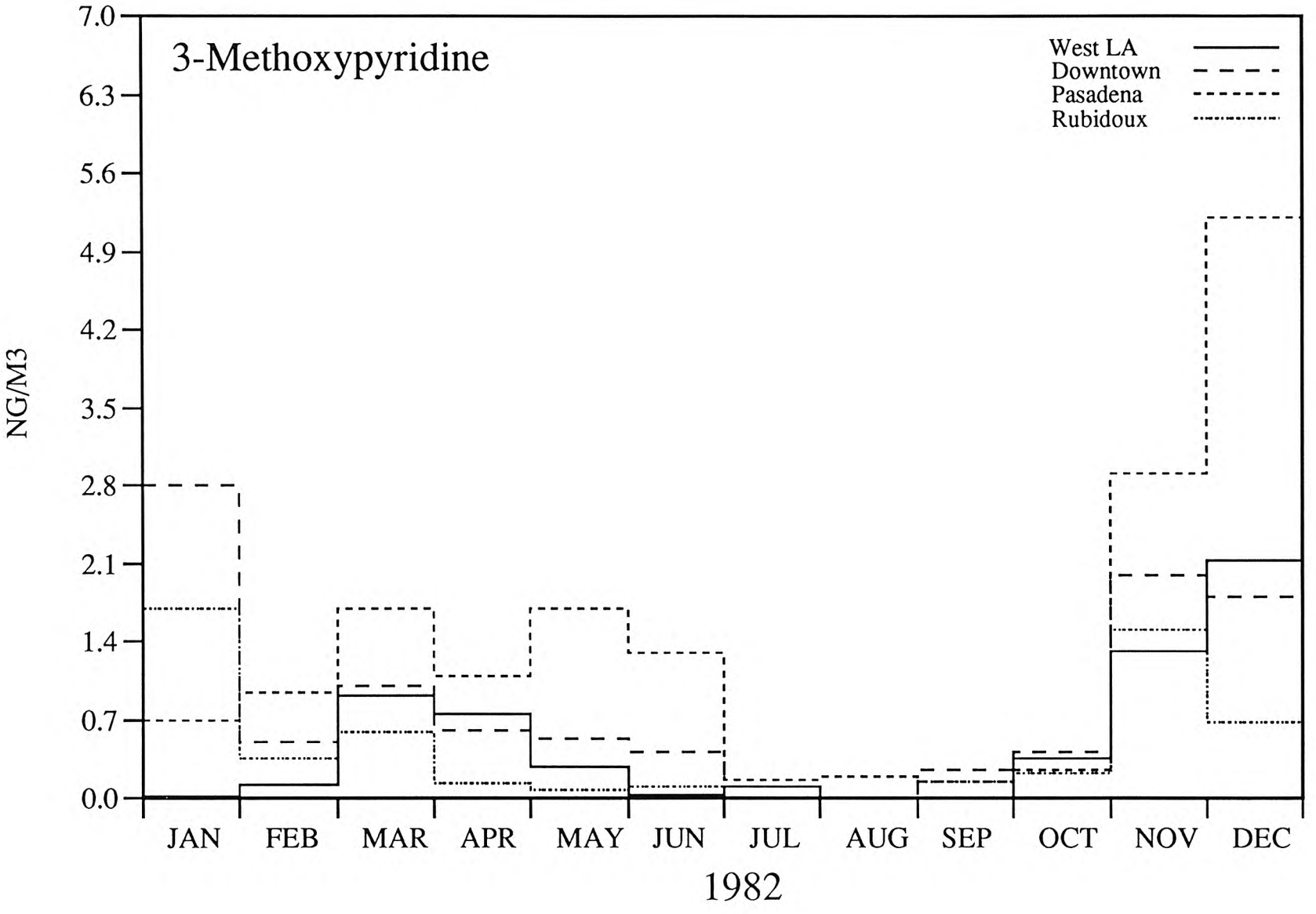

7H-Benz[de]anthracen-7-one
West LA
Downtown
Pasadena
Rubidoux
NG/M3
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

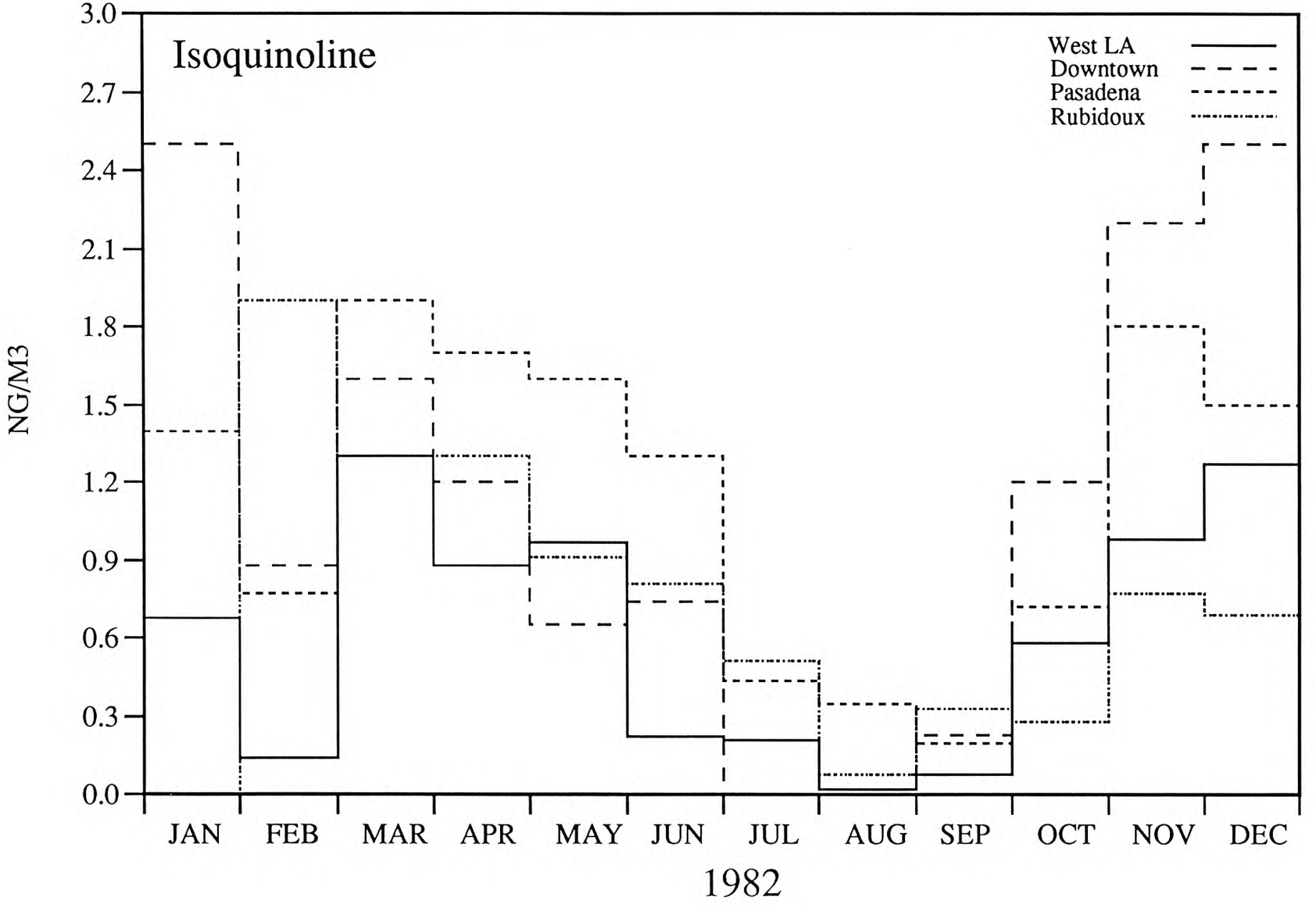

Benz[a]anthracene-7,12-dione
West LA
Downtown
Pasadena
Rubidoux
NG/M3
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

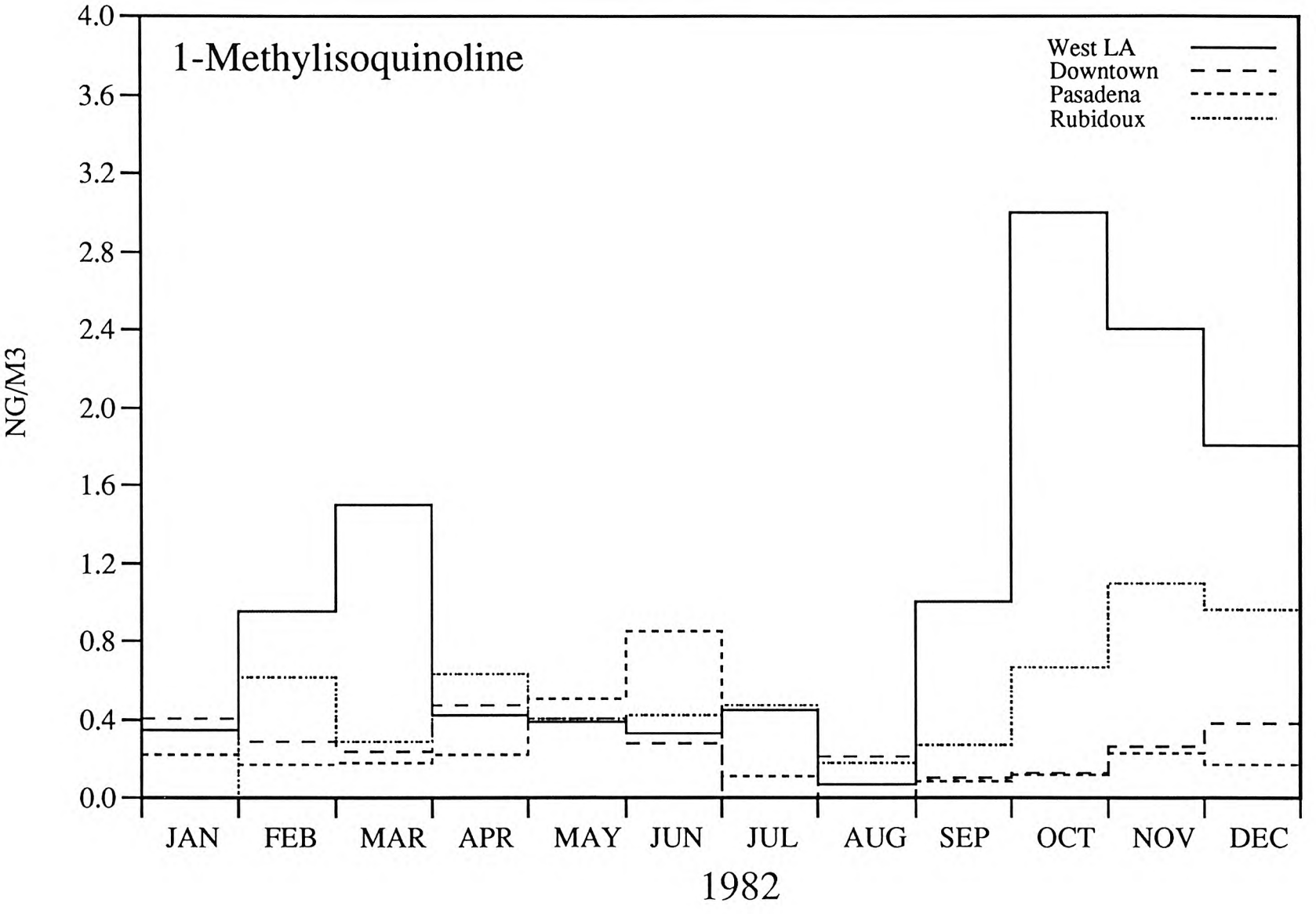

Benzo[cd]pyrenone
West LA
Downtown
Pasadena
Rubidoux
NG/M3
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

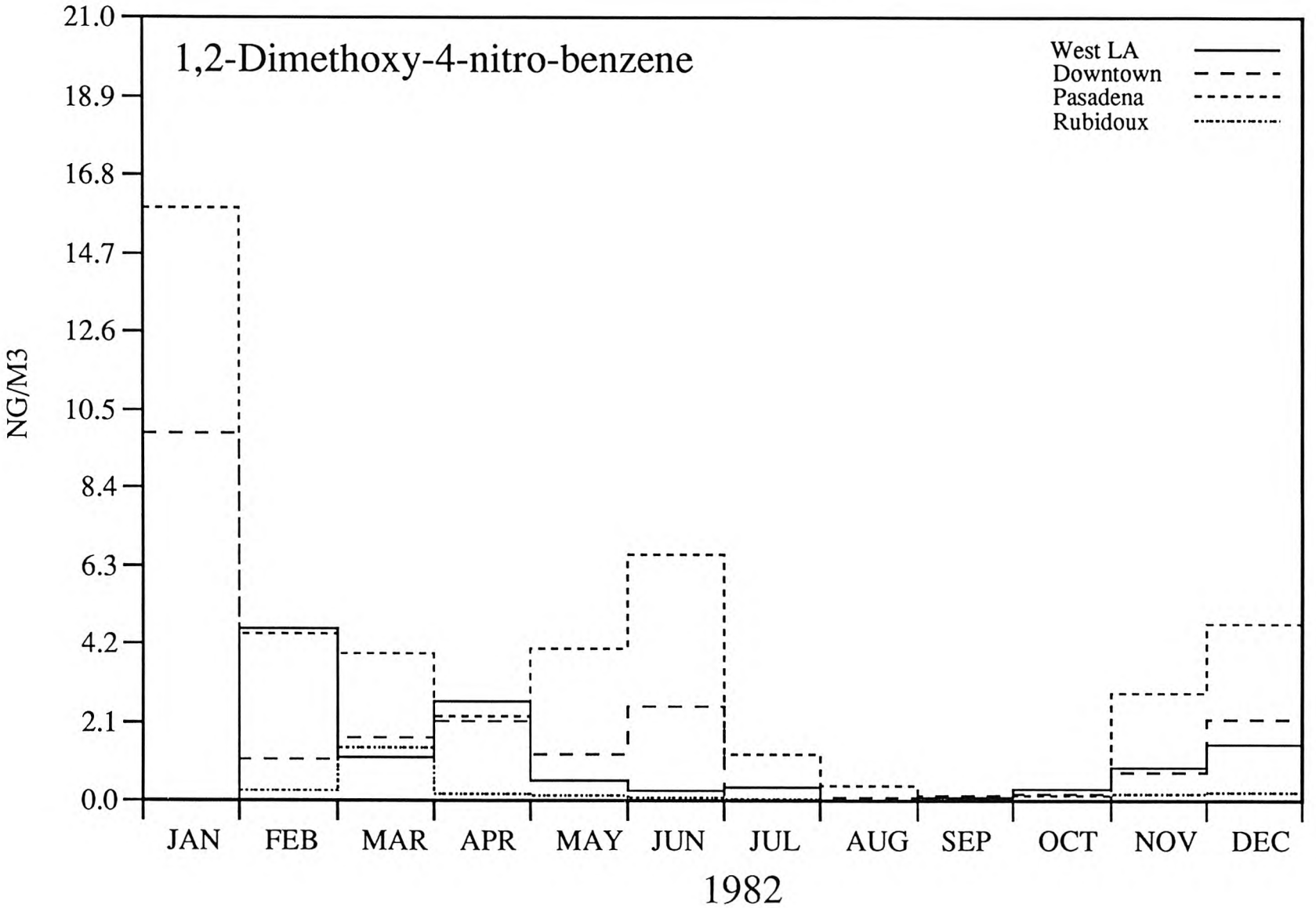
Appendix A10

Ambient Concentration Profiles for N-Containing Compounds


3-Methoxypyridine
West LA
Downtown
Pasadena
Rubidoux
NG/M3
7.0
6.3
5.6
4.9
4.2
3.5
2.8
2.1
1.4
0.7
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

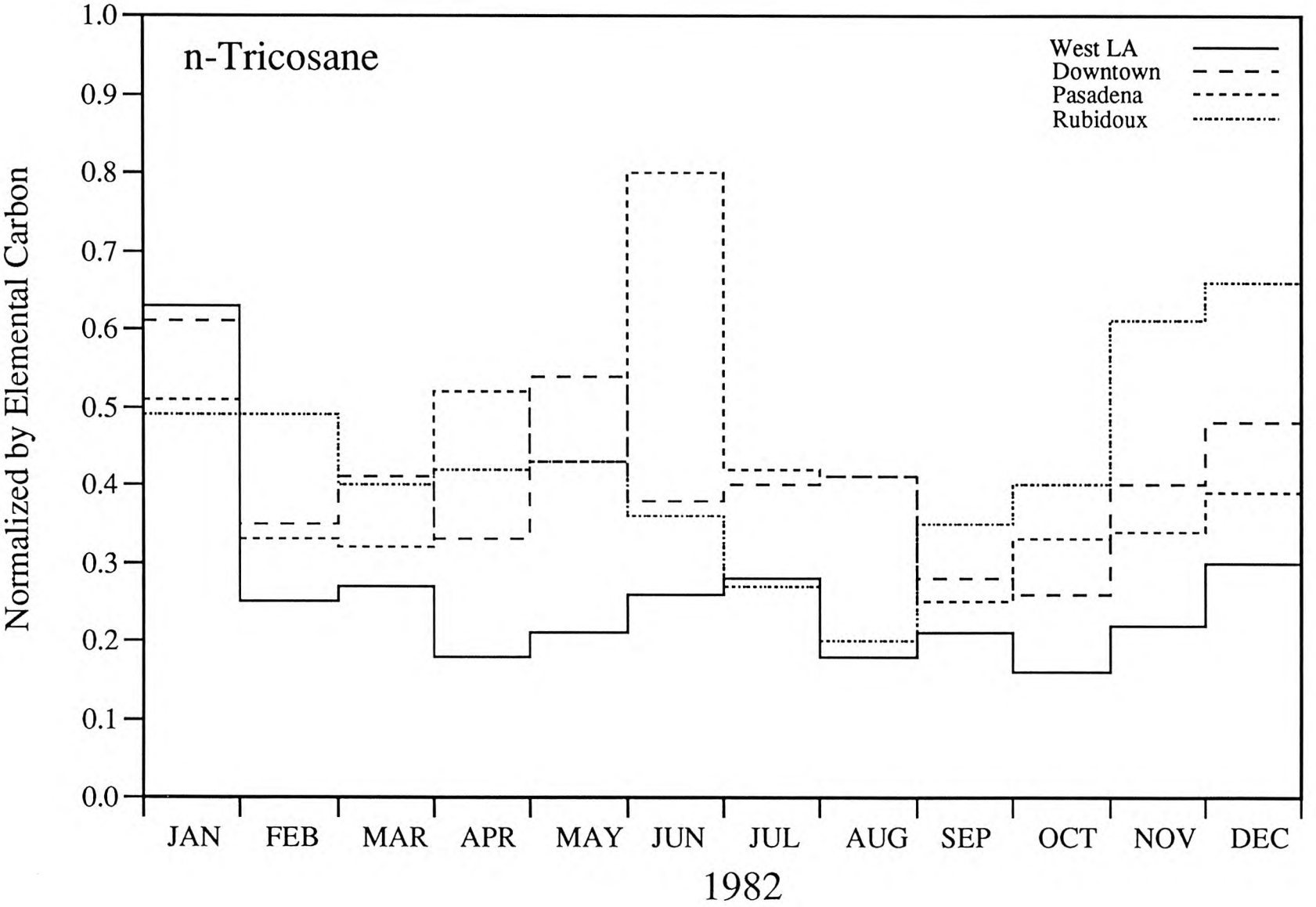

Isoquinoline
West LA
Downtown
Pasadena
Rubidoux
NG/M3
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

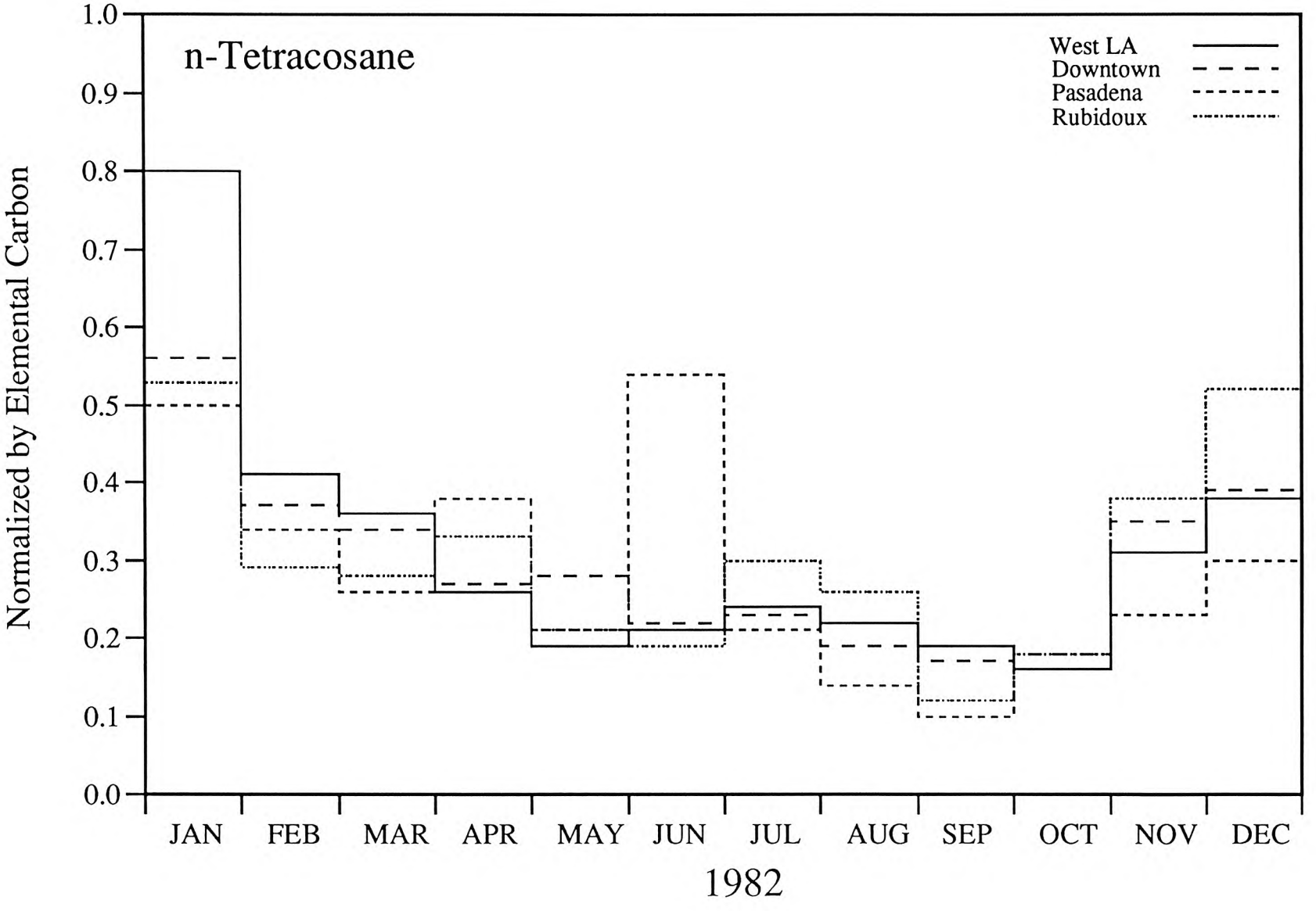

1-Methylisoquinoline
West LA
Downtown
Pasadena
Rubidoux
NG/M3
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

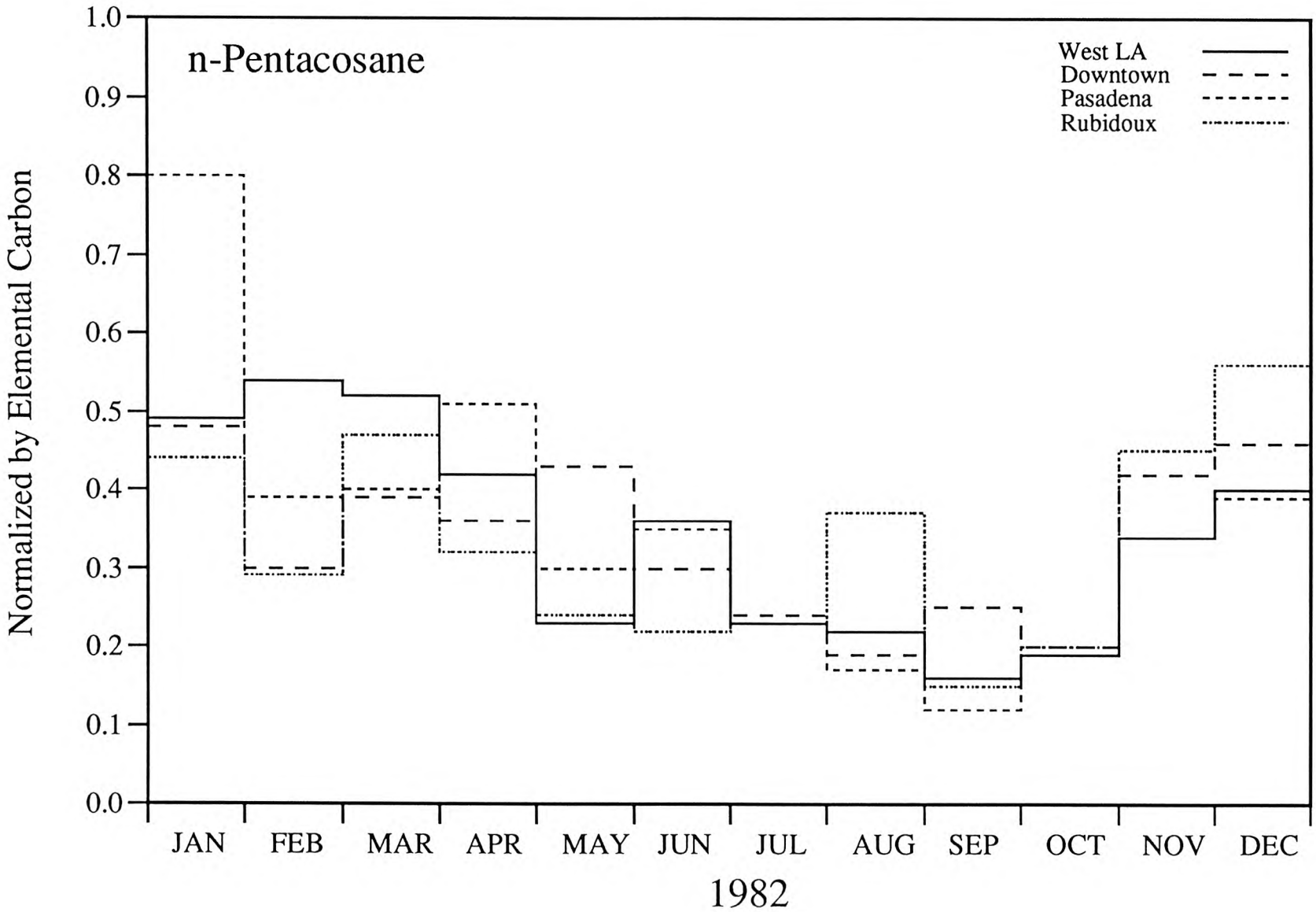

1,2-Dimethoxy-4-nitro-benzene
West LA
Downtown
Pasadena
Rubidoux
NG/M3
21.0
18.9
16.8
14.7
12.6
10.5
8.4
6.3
4.2
2.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

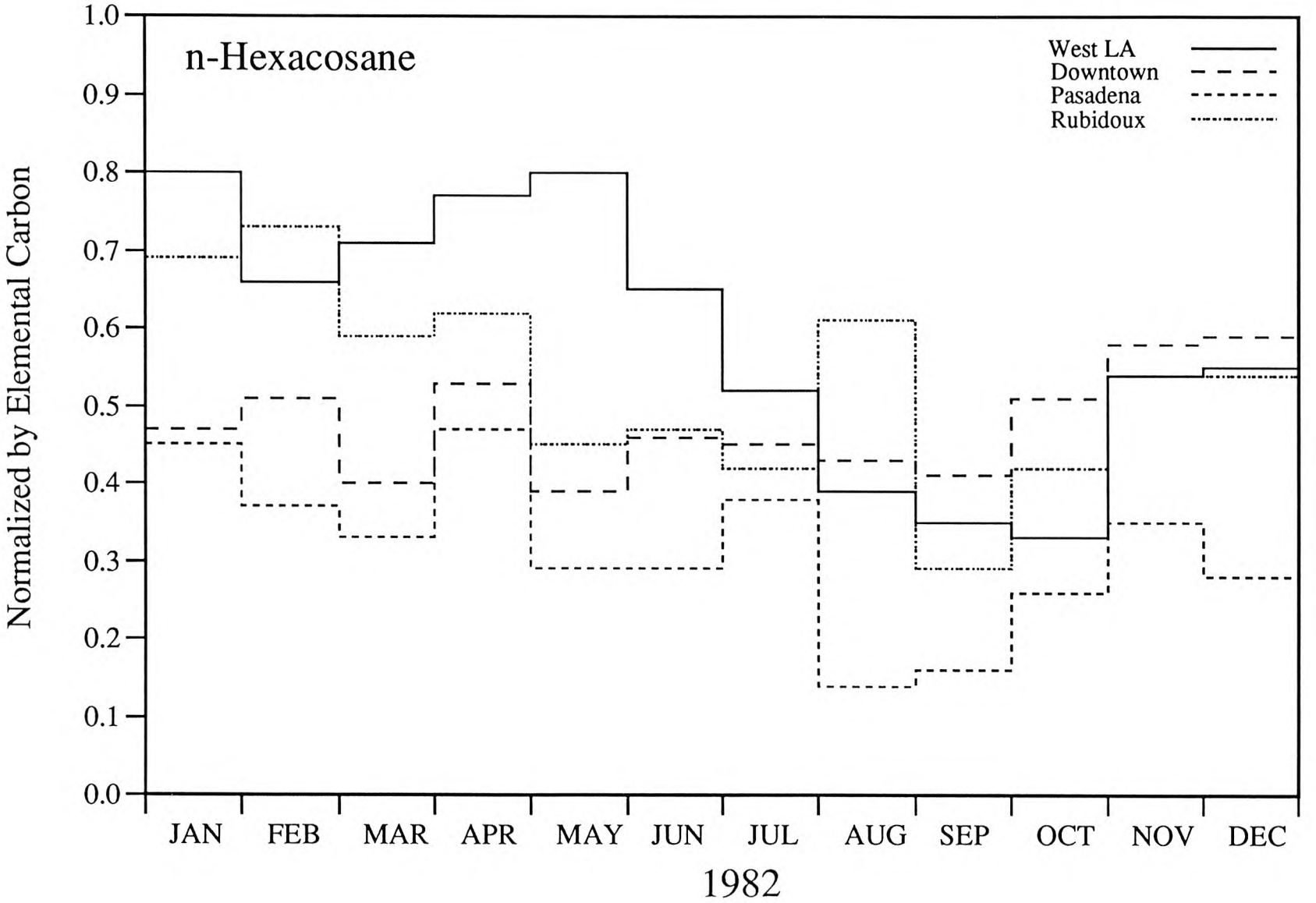
Appendix B1

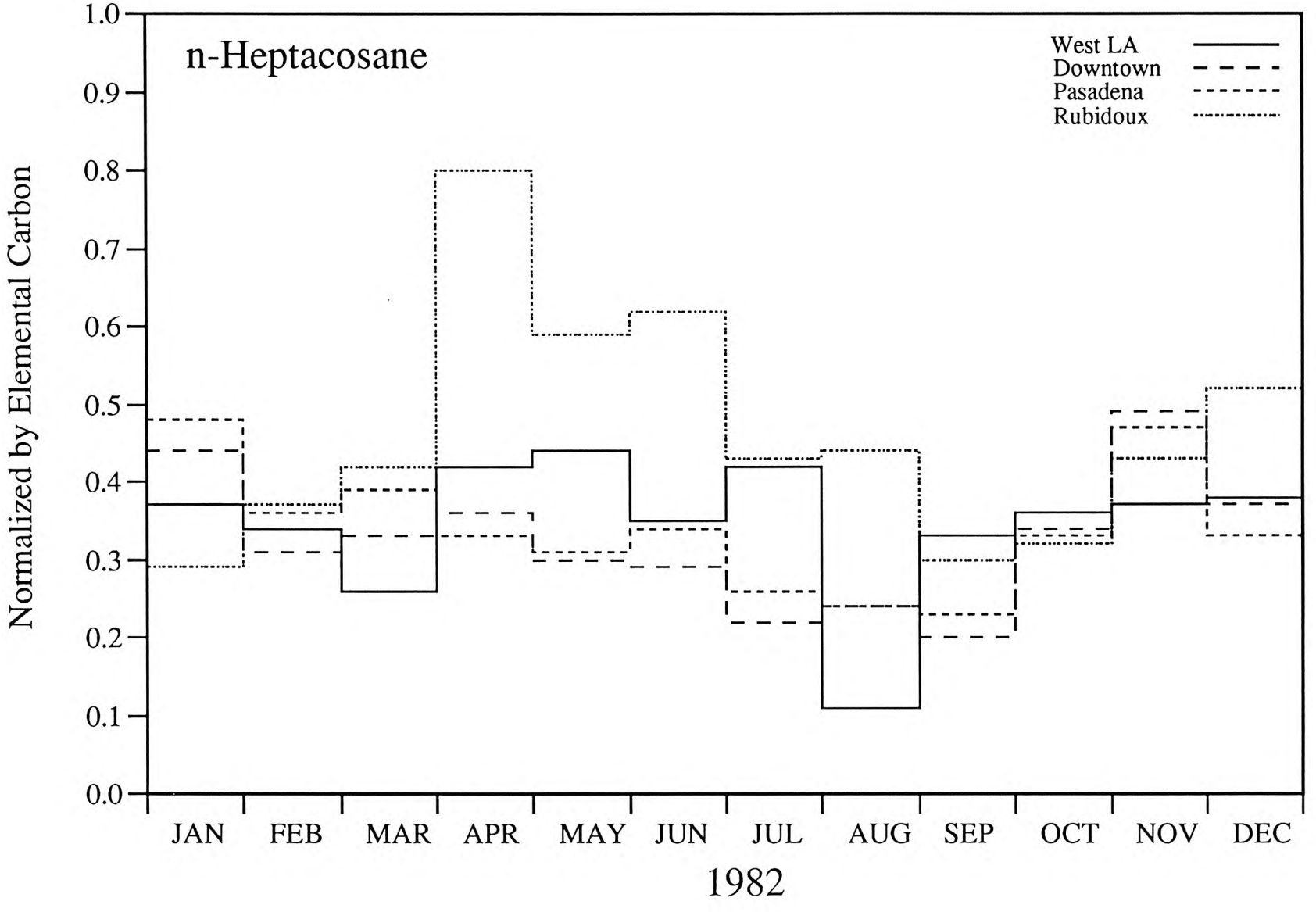
Normalized Concentration Profiles for n-Alkanes

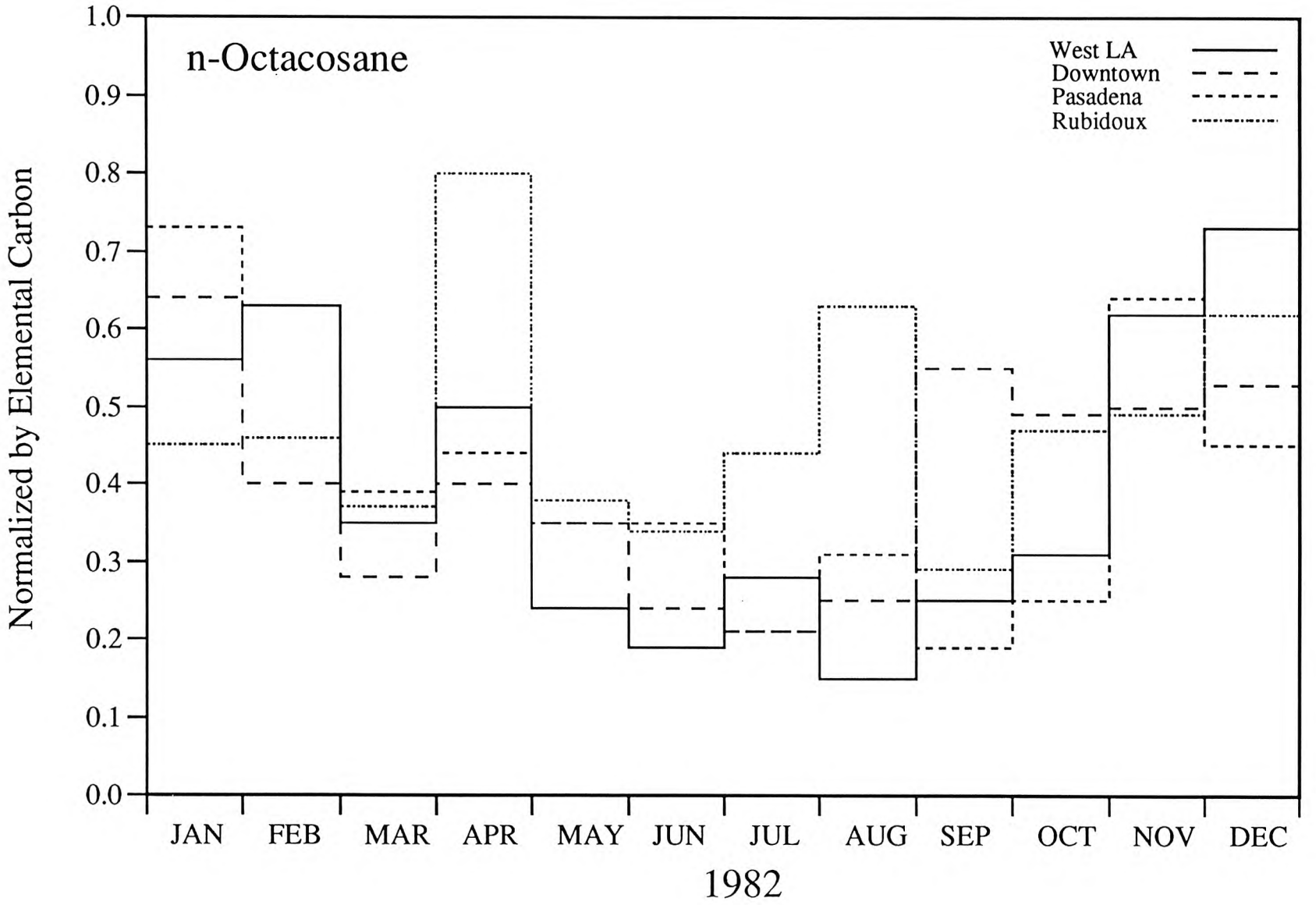

n-Tricosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

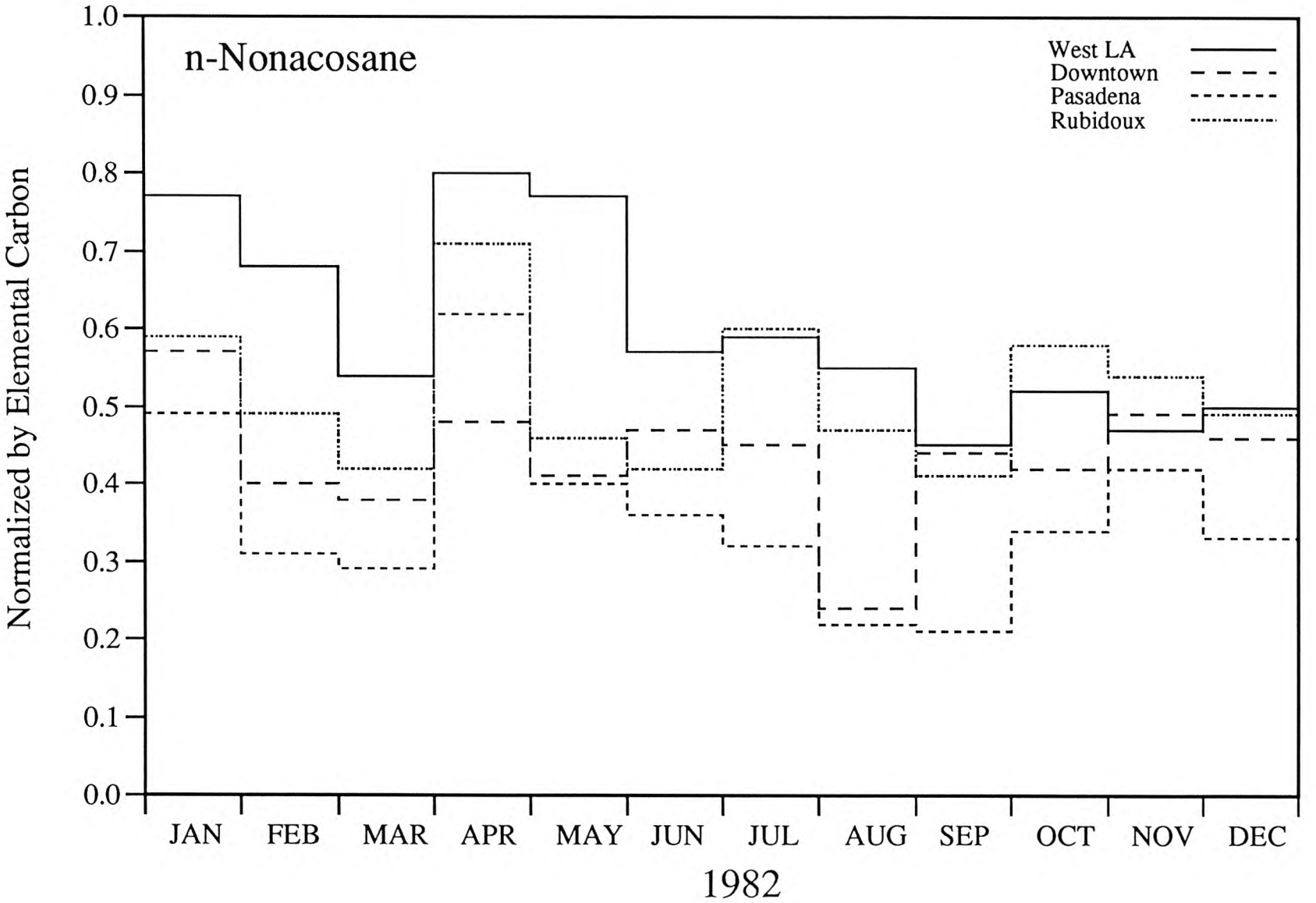

n-Tetracosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

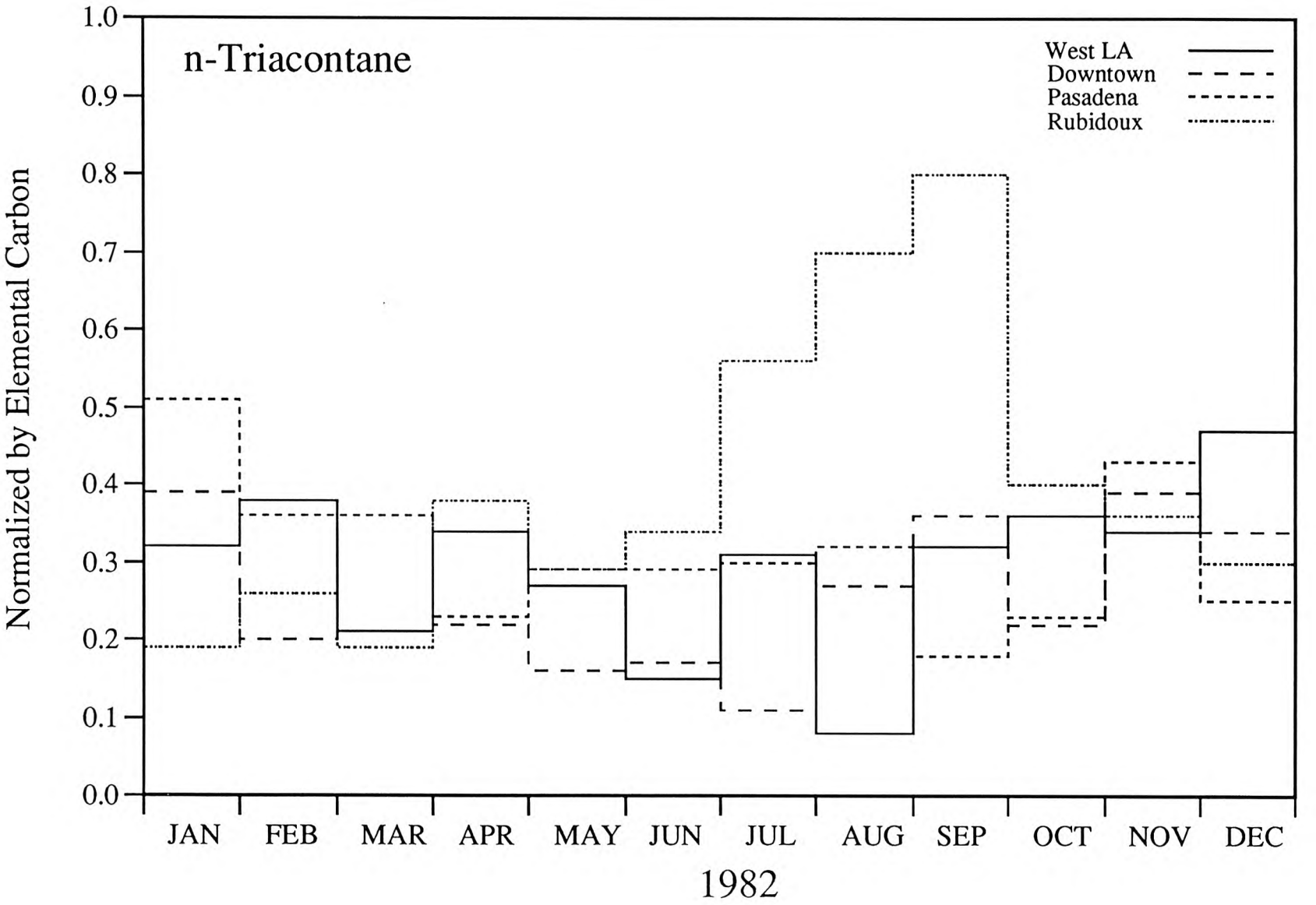

n-Pentacosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

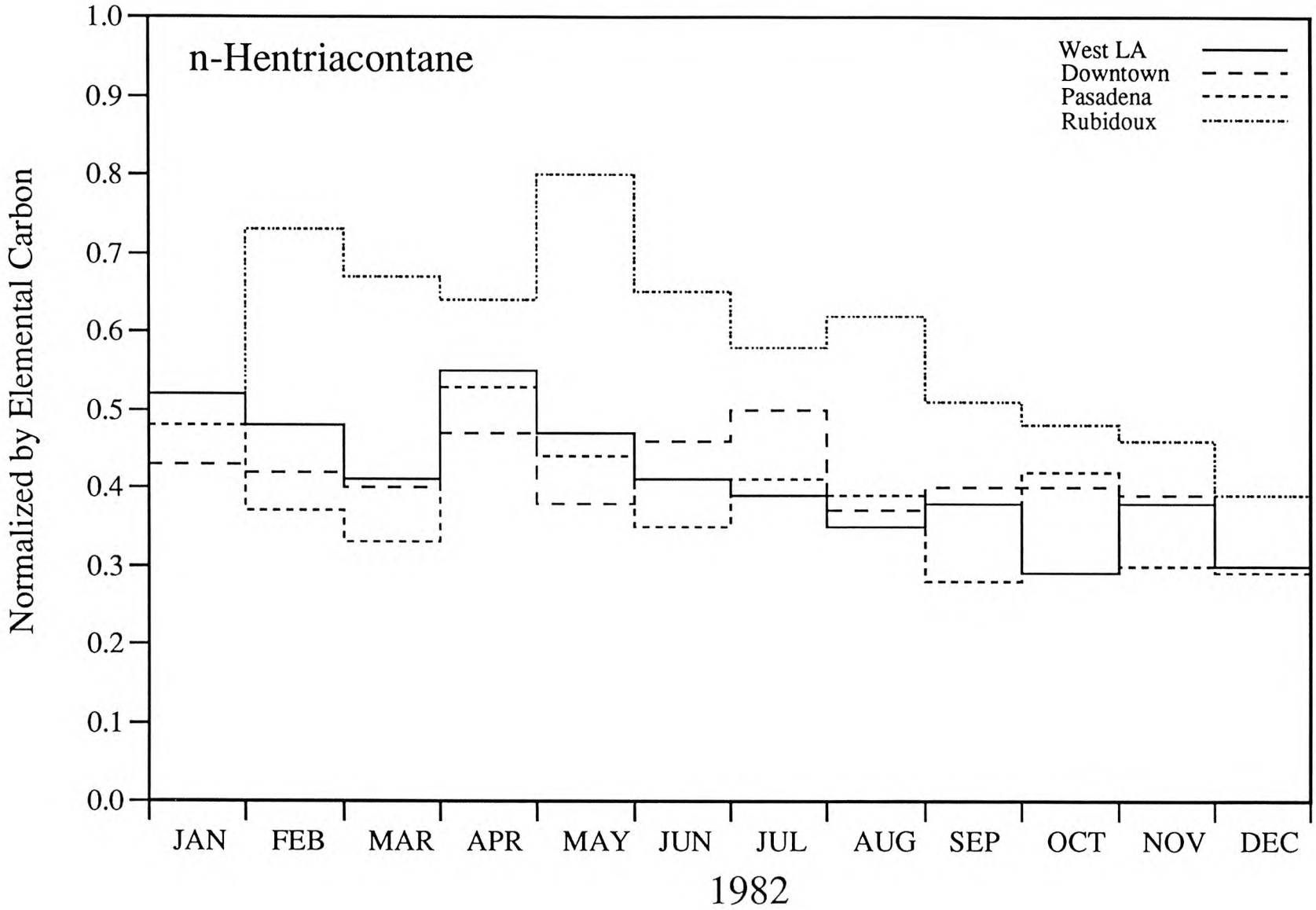

n-Hexacosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

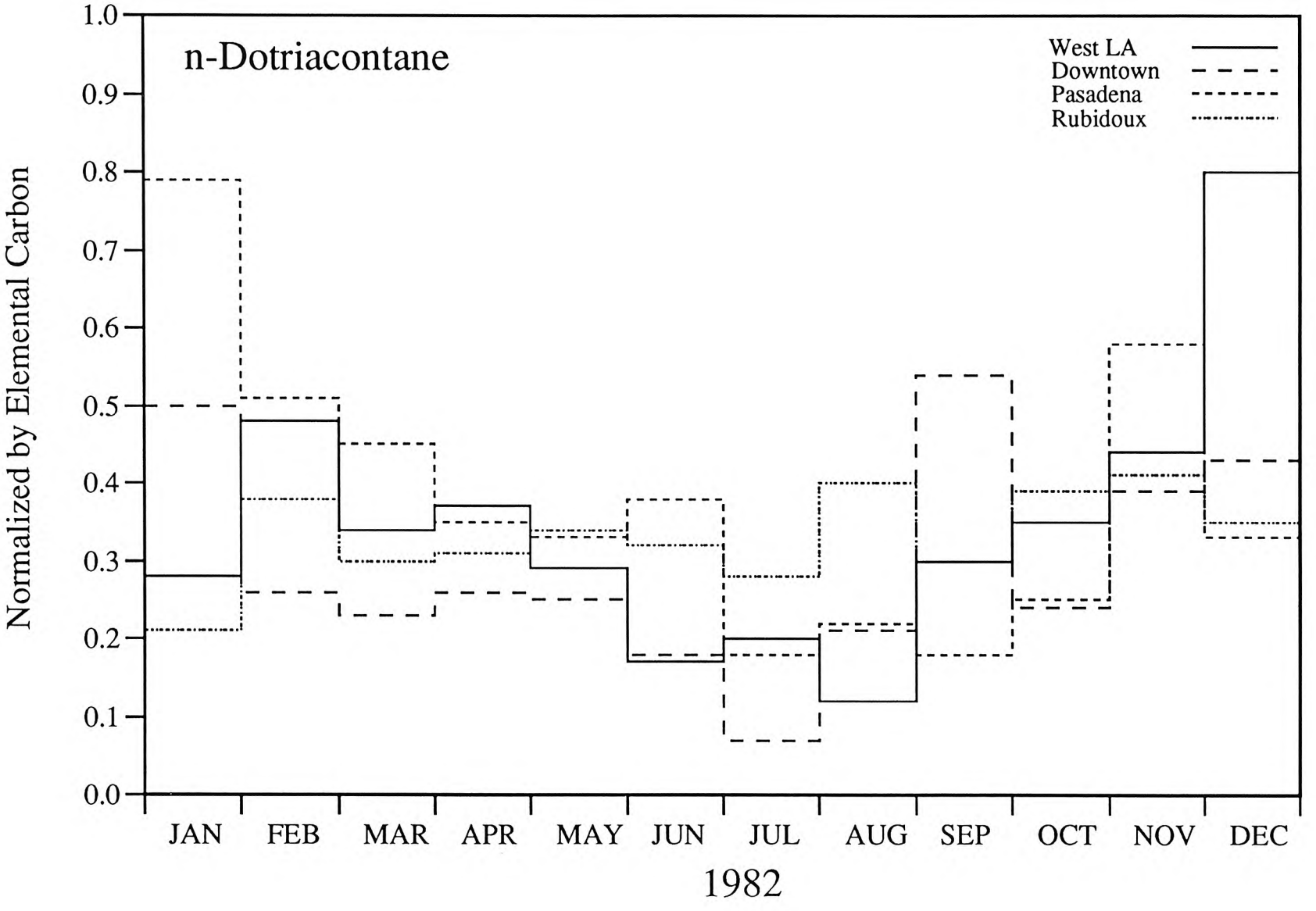

n-Heptacosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

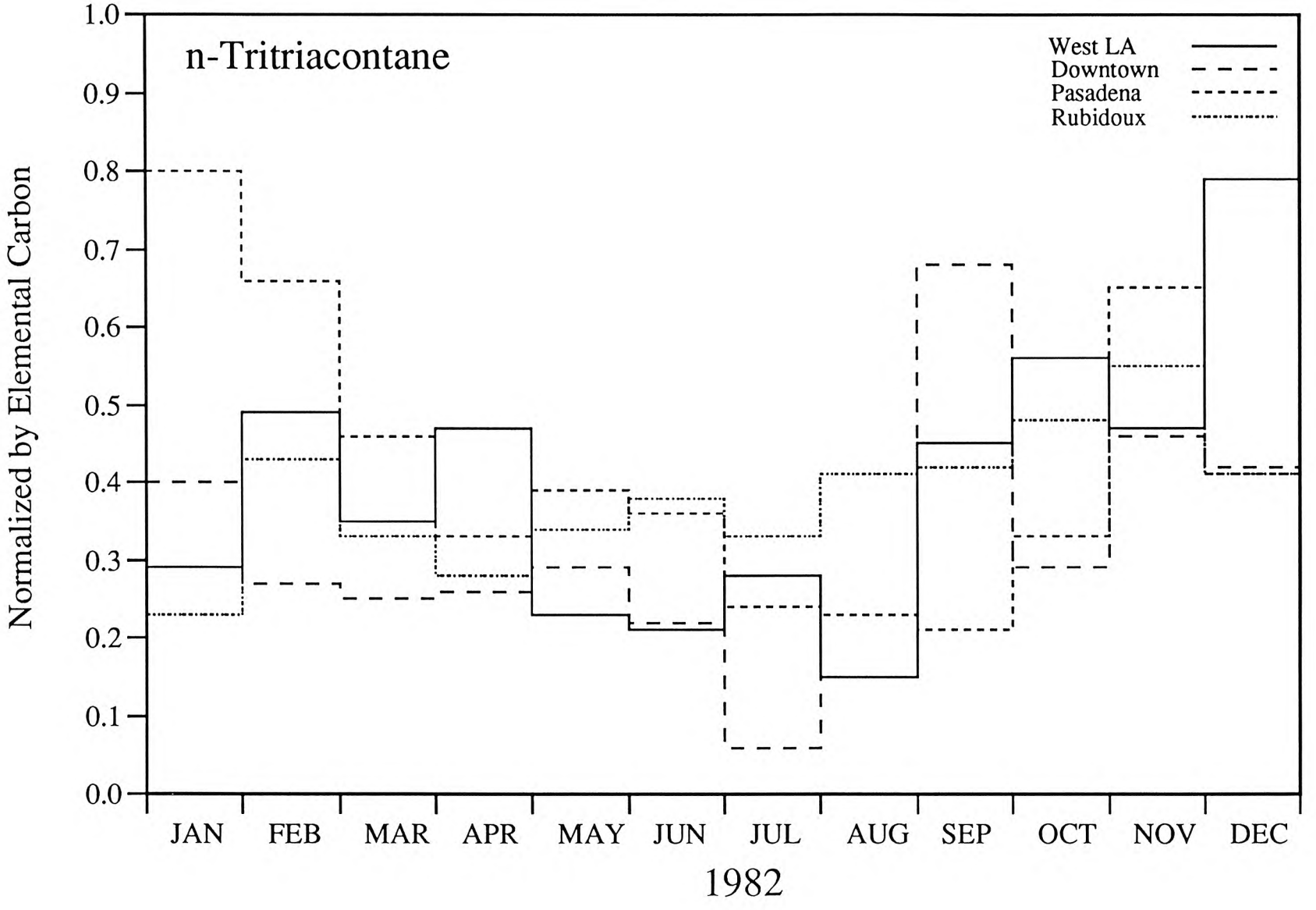

n-Octacosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

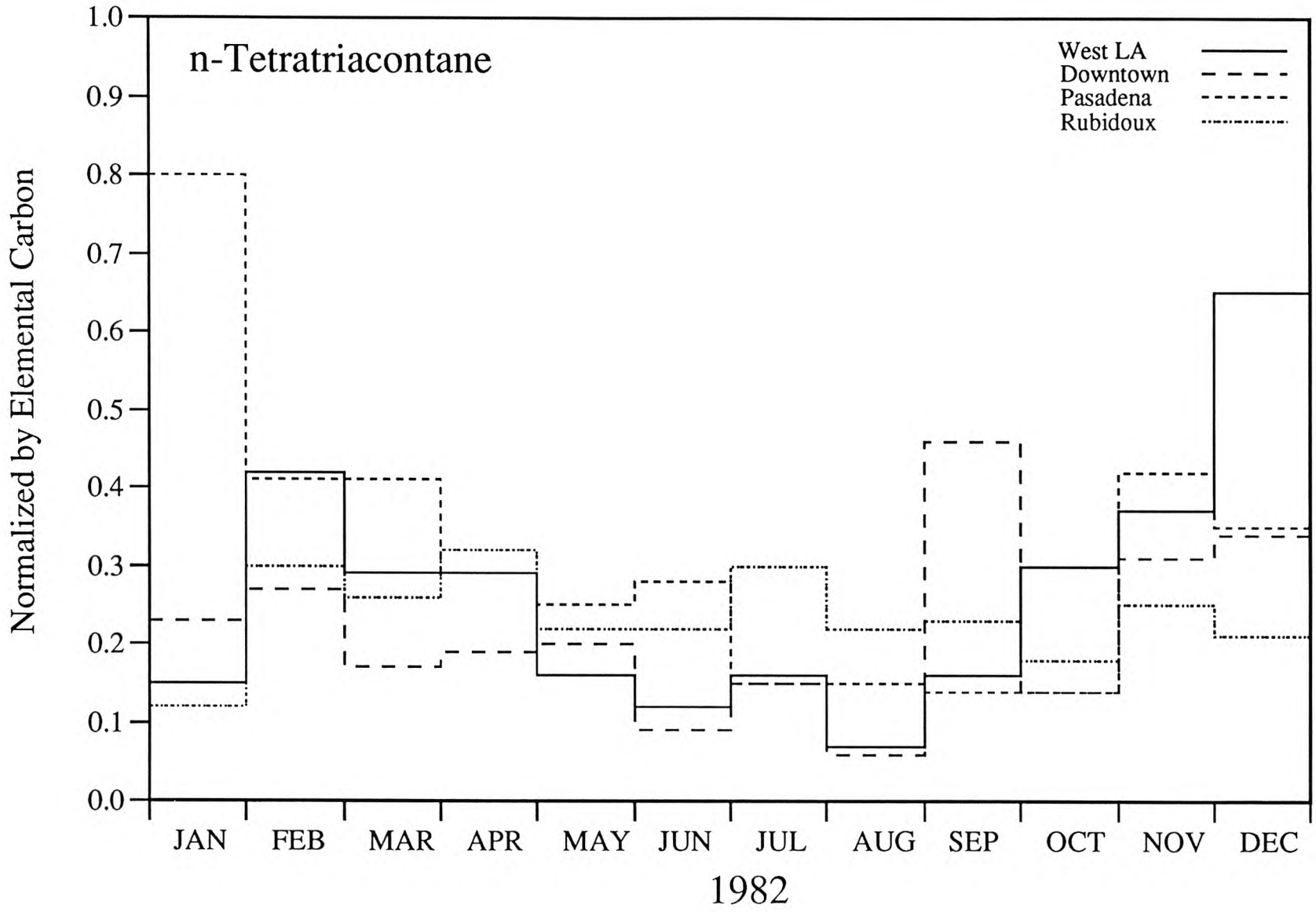

n-Nonacosane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Triacontane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Hentriacontane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

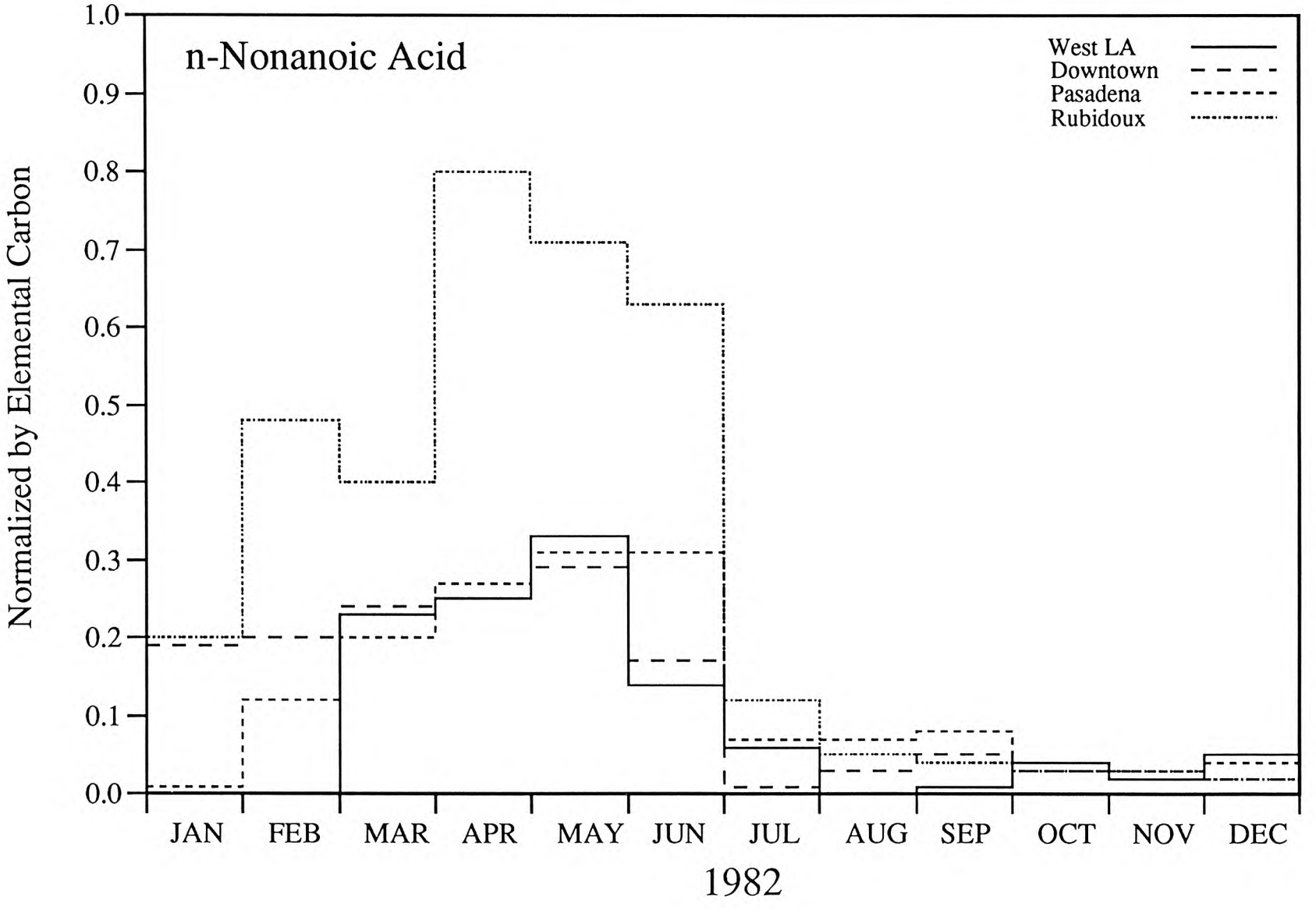

n-Dotriacontane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

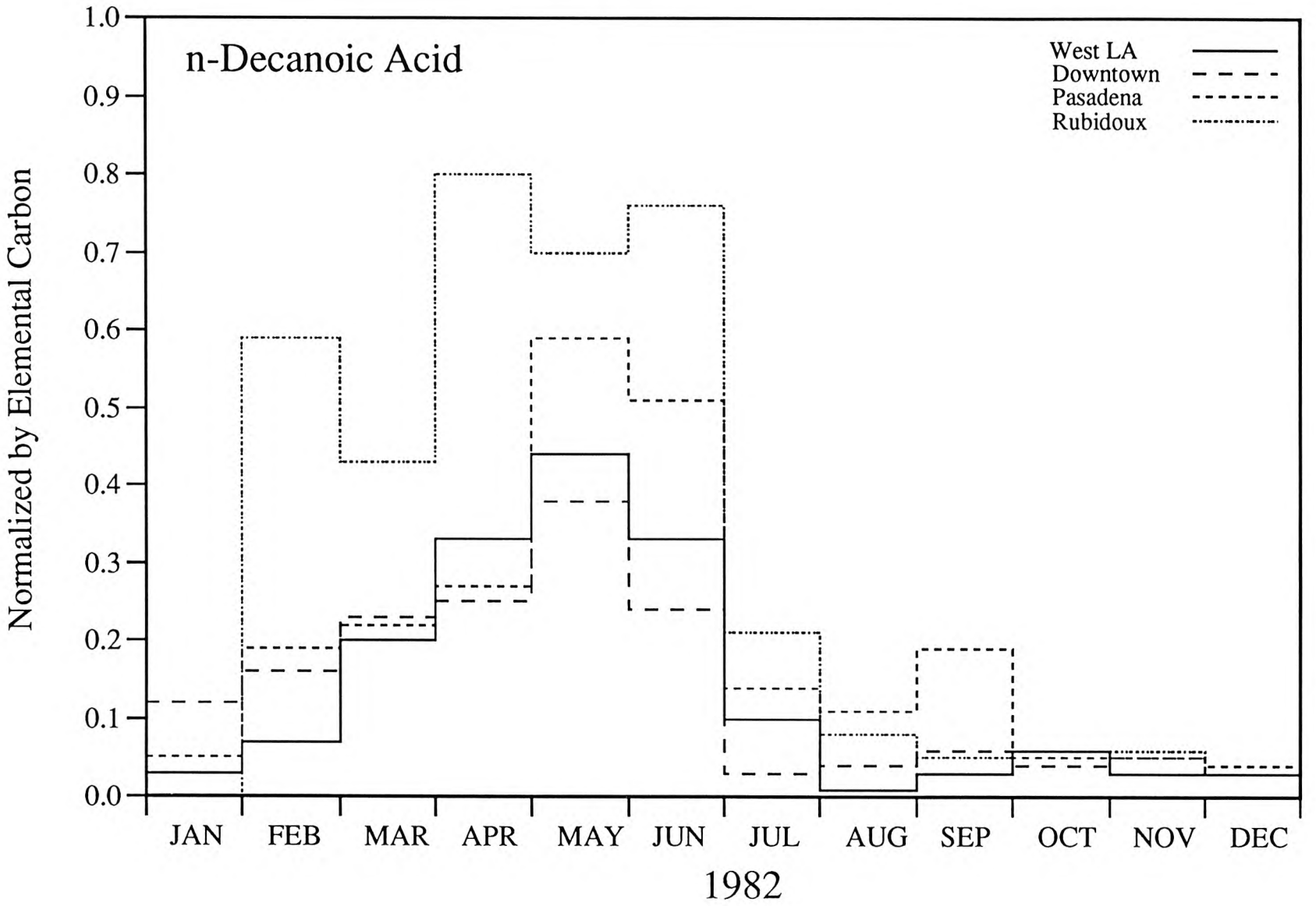

n-Tritriacontane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

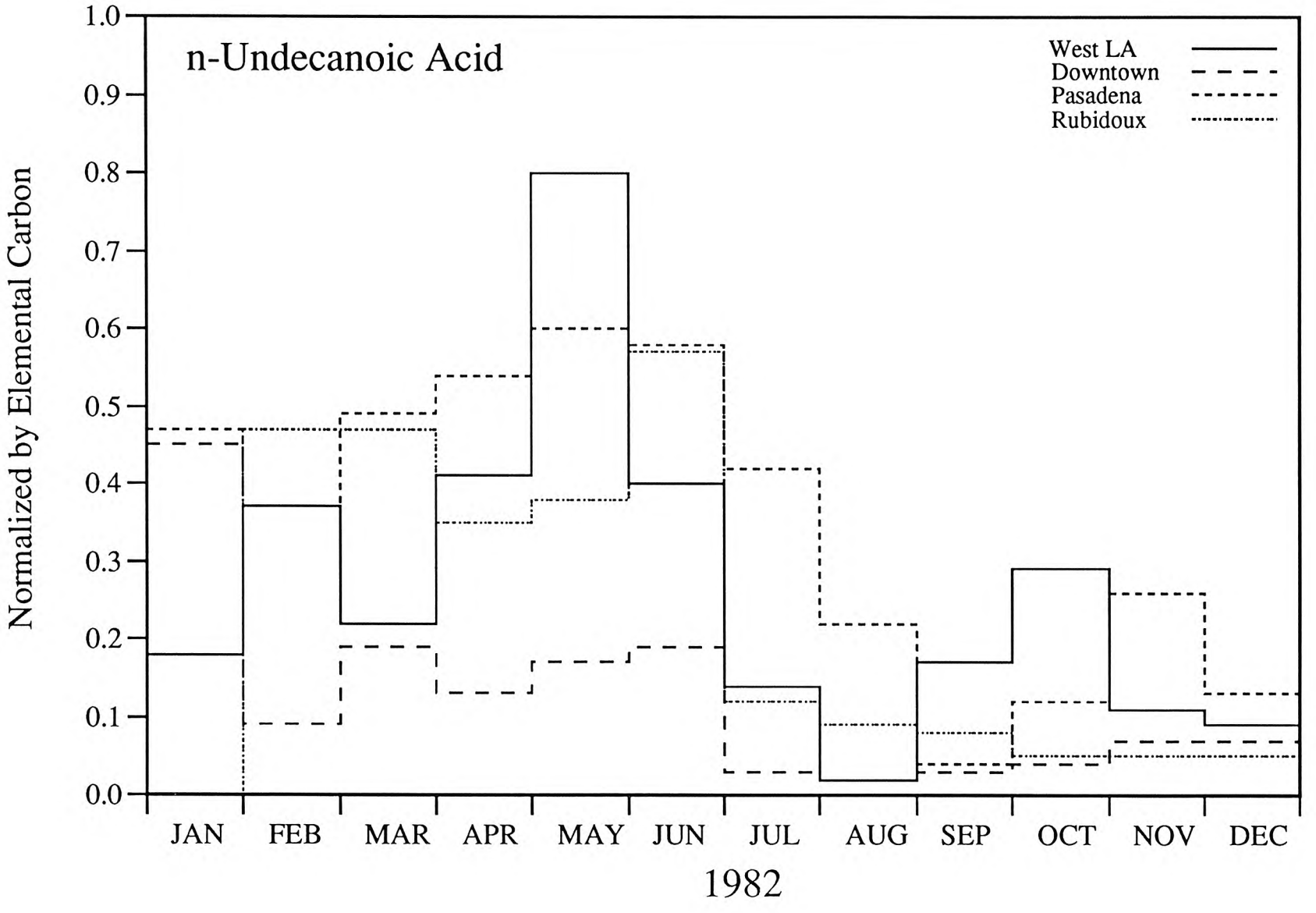

n-Tetratriacontane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

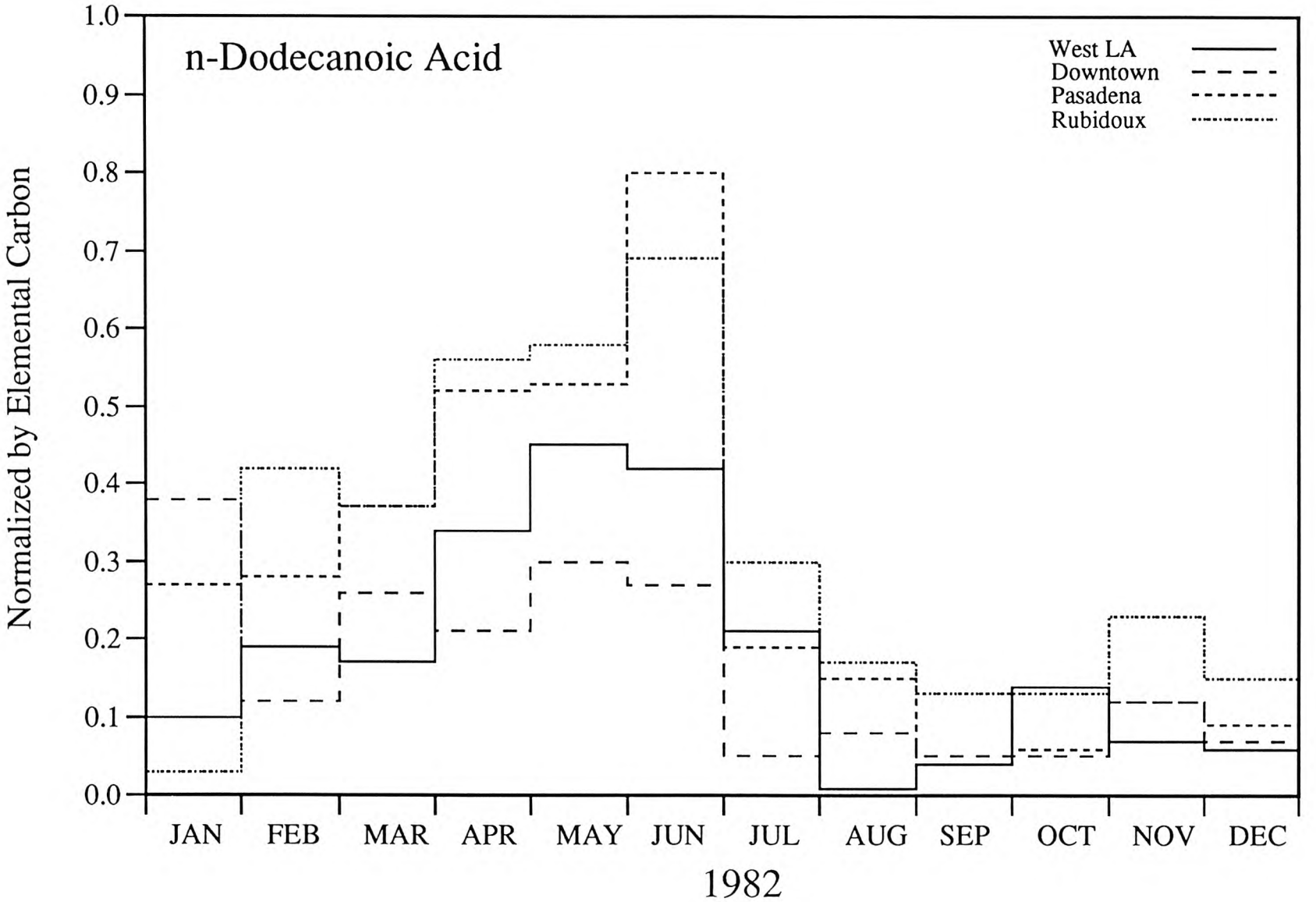
Appendix B2

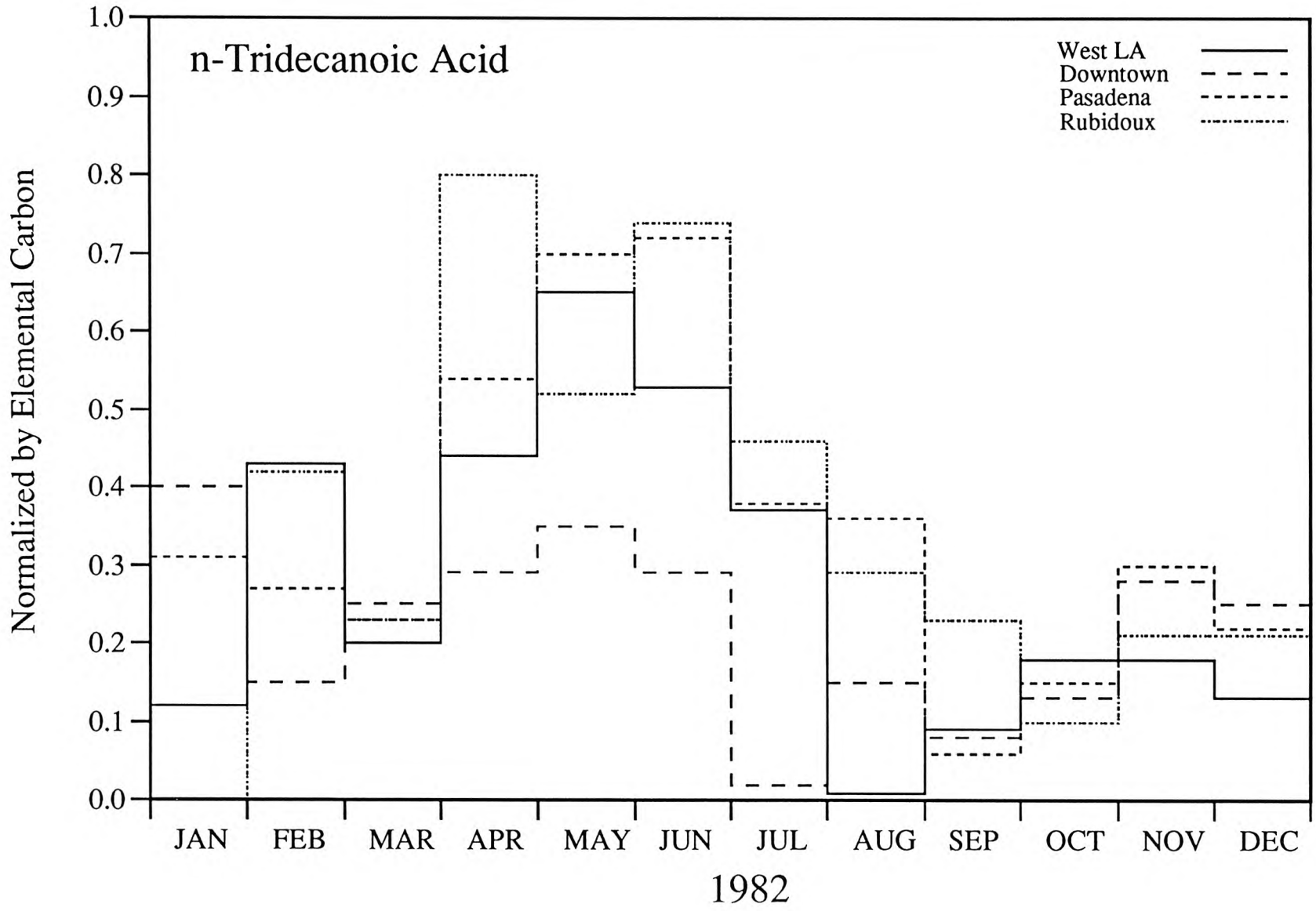
Normalized Concentration Profiles for n-Alkanoic Acids

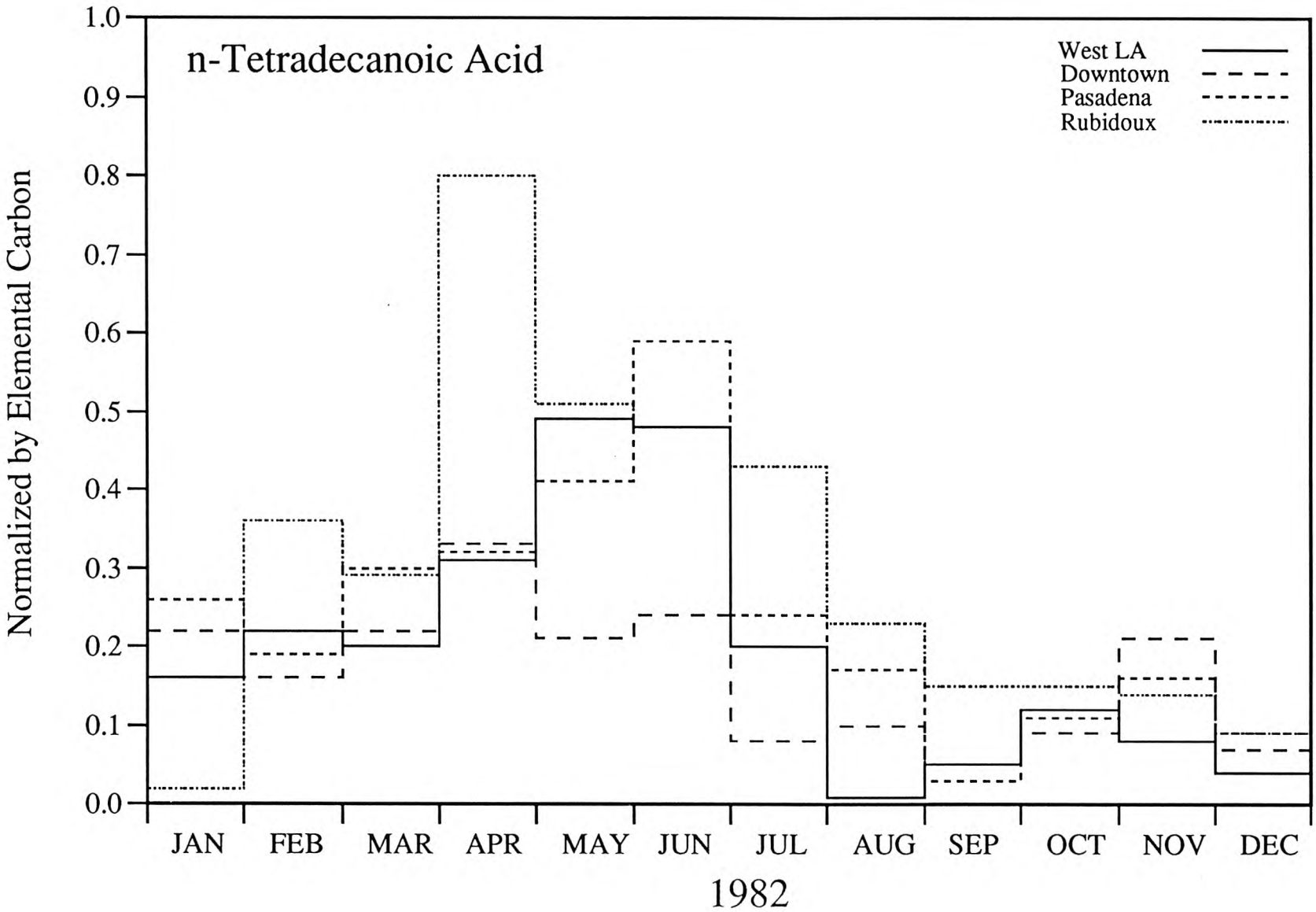

n-Nonanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

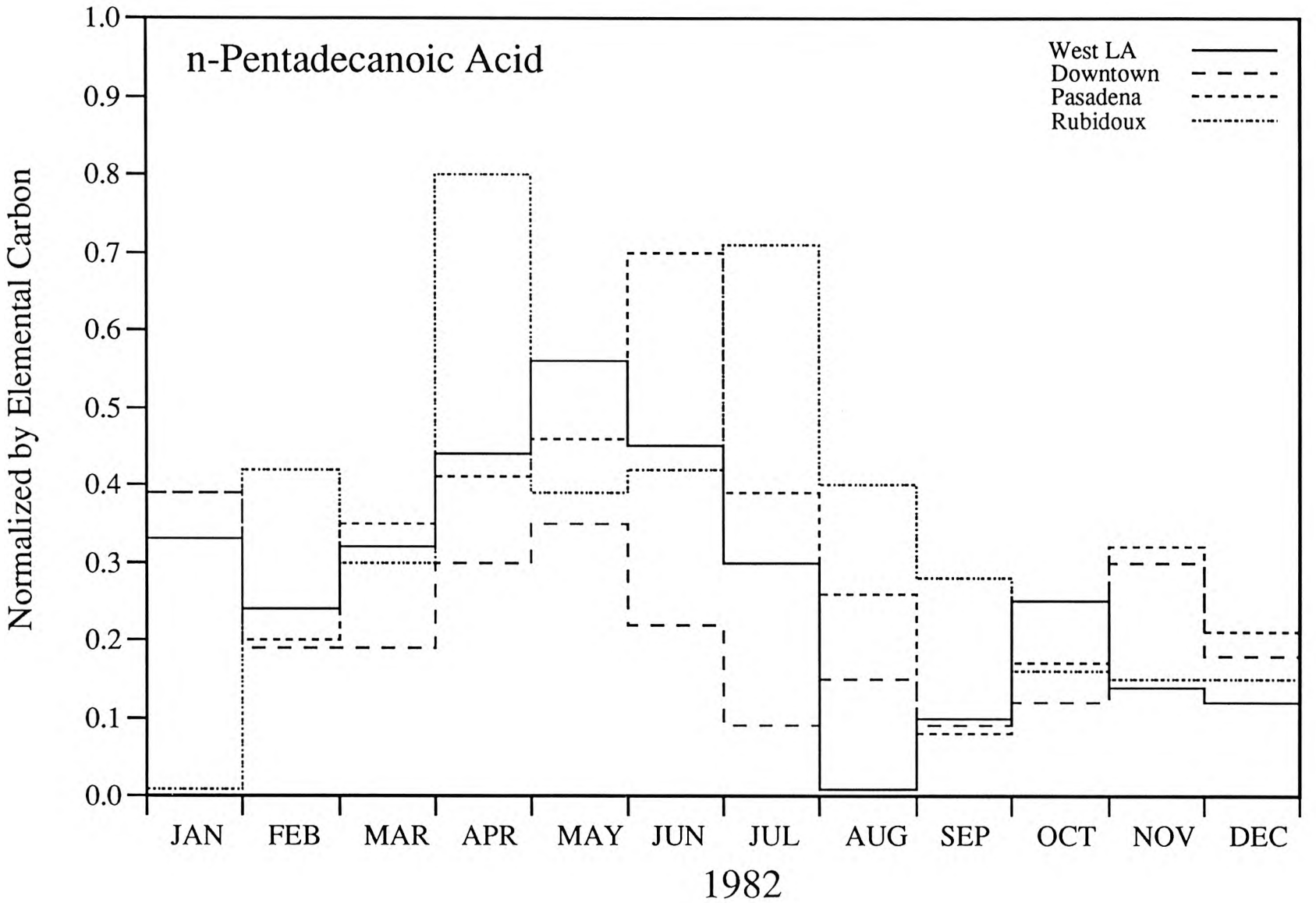

n-Decanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

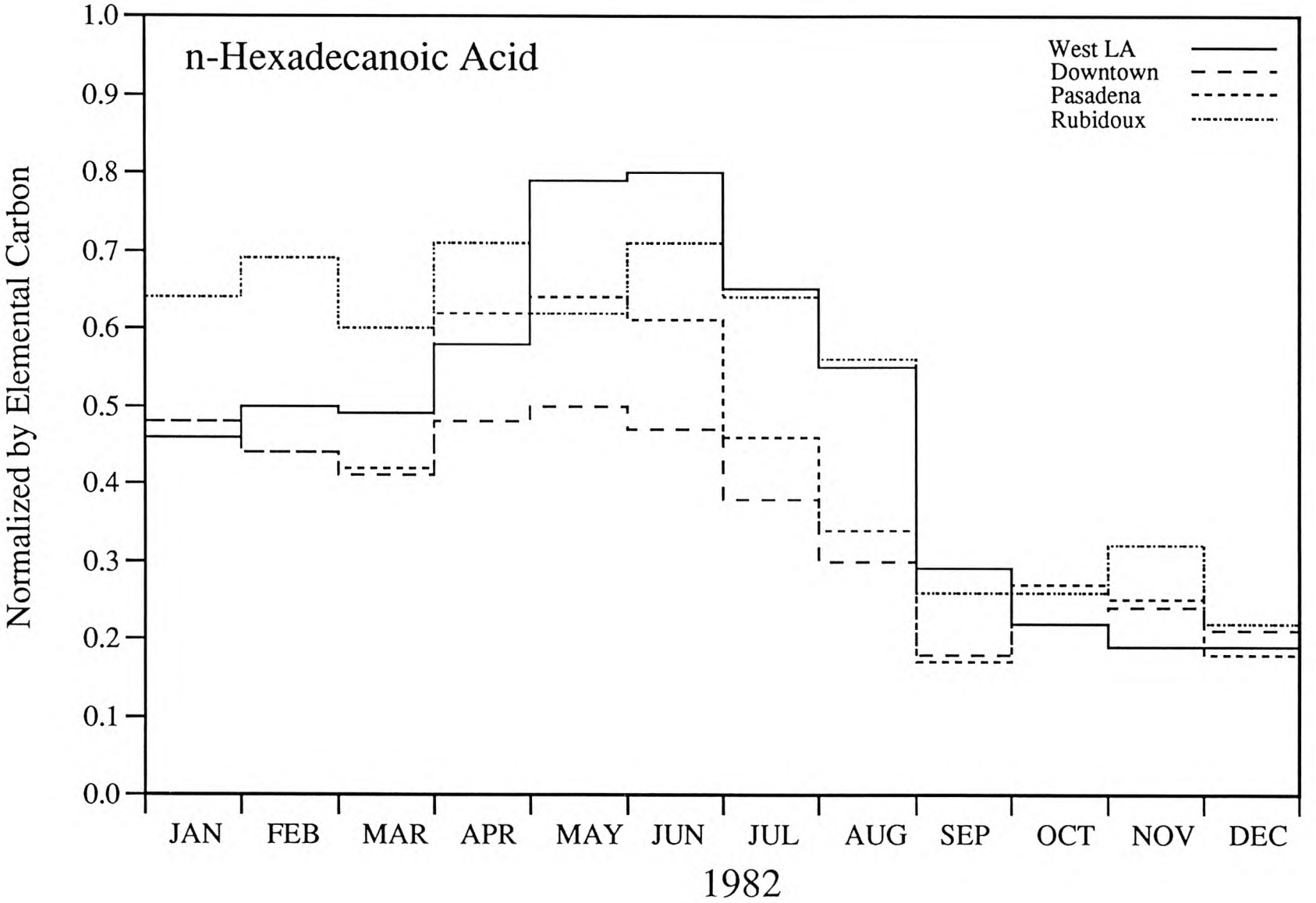

n-Undecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Dodecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Tridecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Tetradecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Pentadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Hexadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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MAY
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JUL
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SEP
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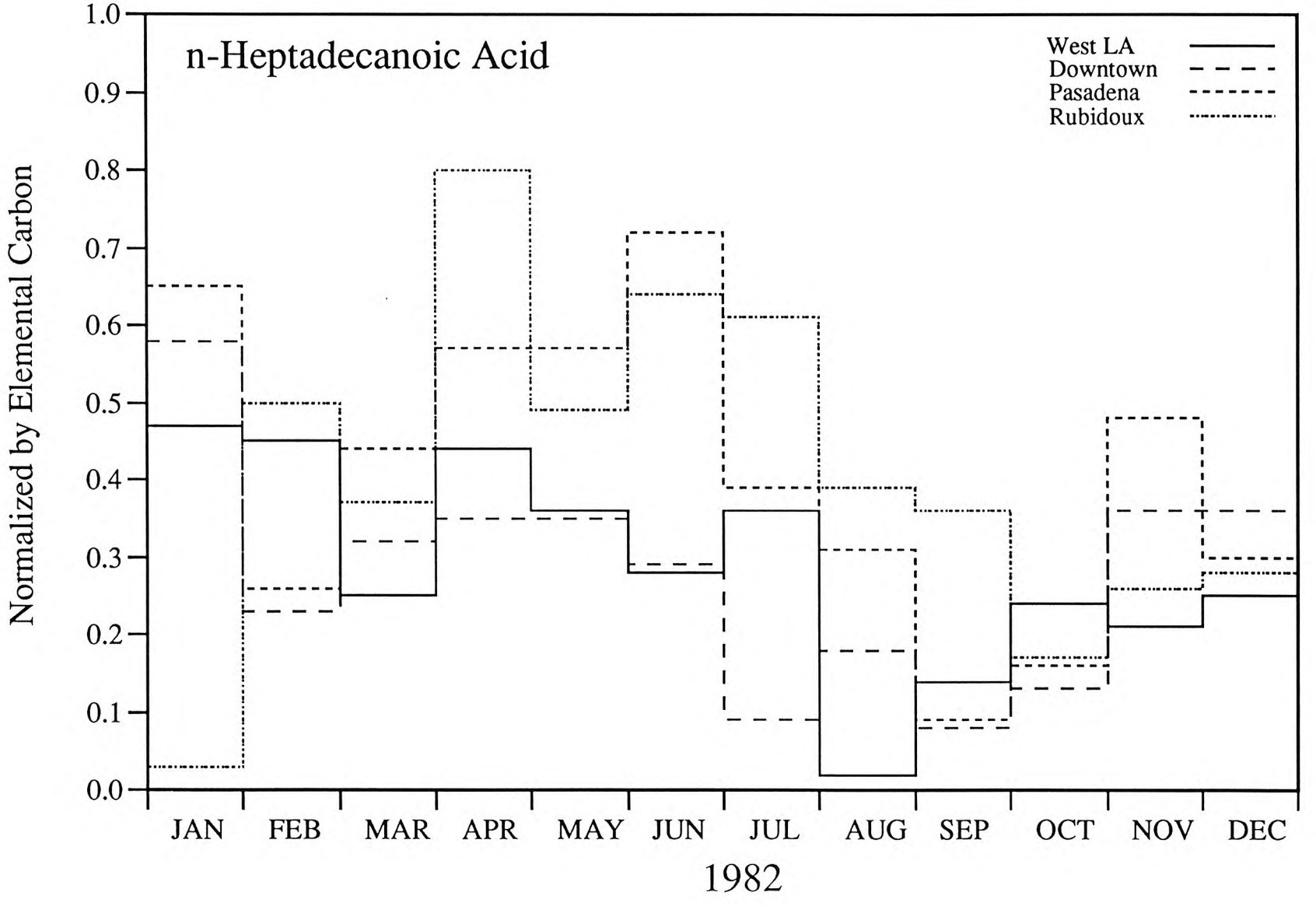
NOV
DEC
1982


n-Heptadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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MAY
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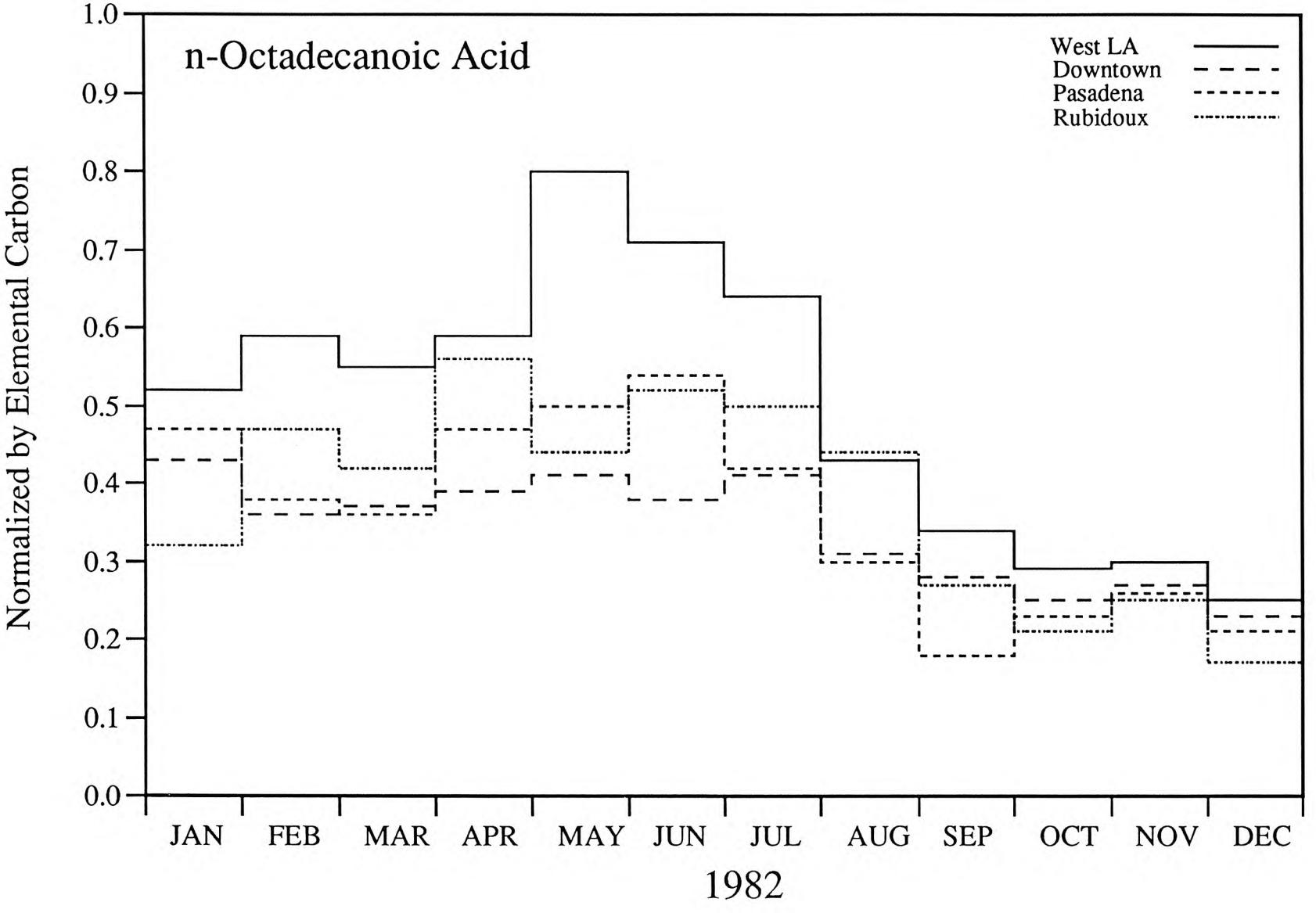
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Octadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
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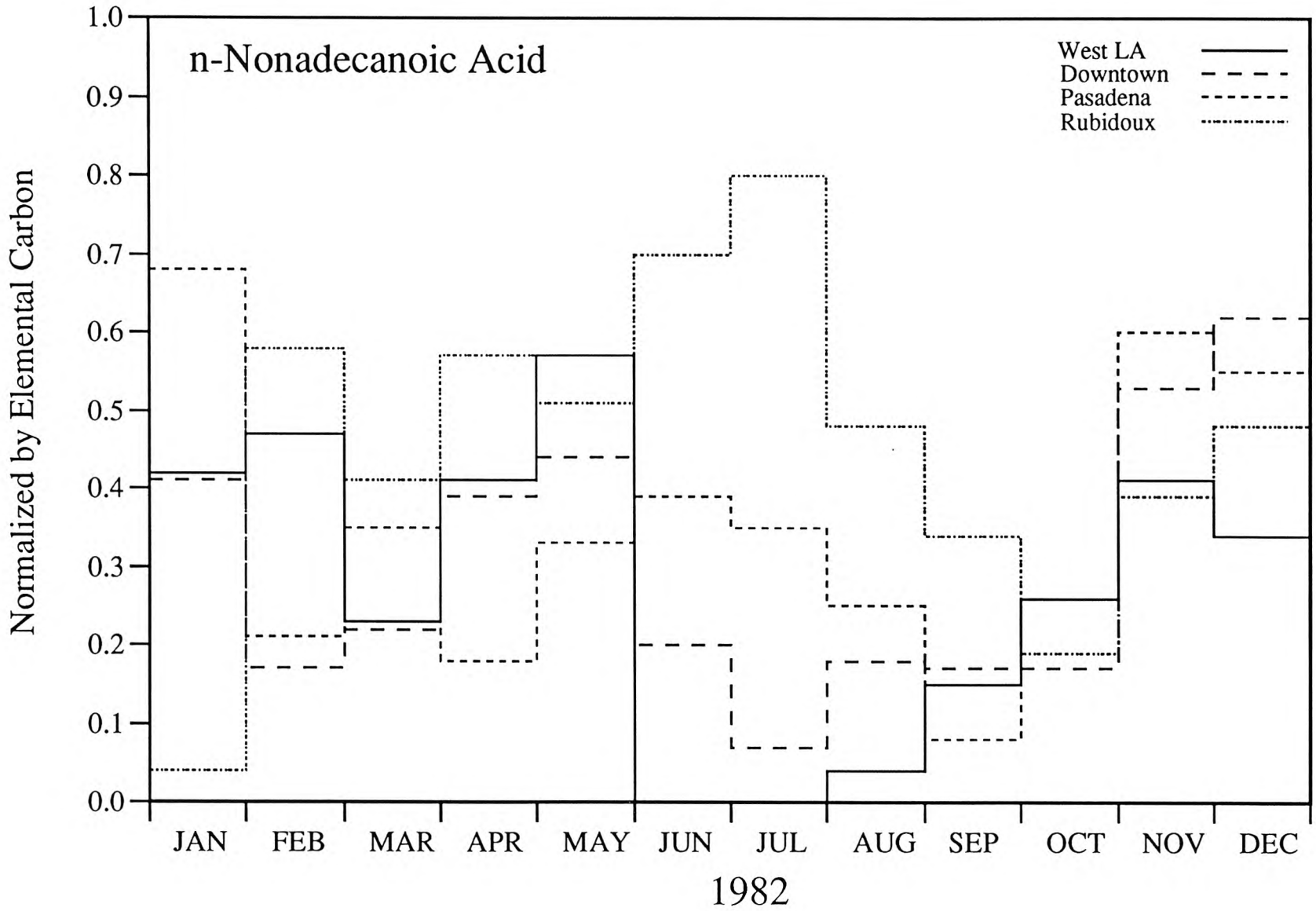
OCT
NOV
DEC
1982


n-Nonadecanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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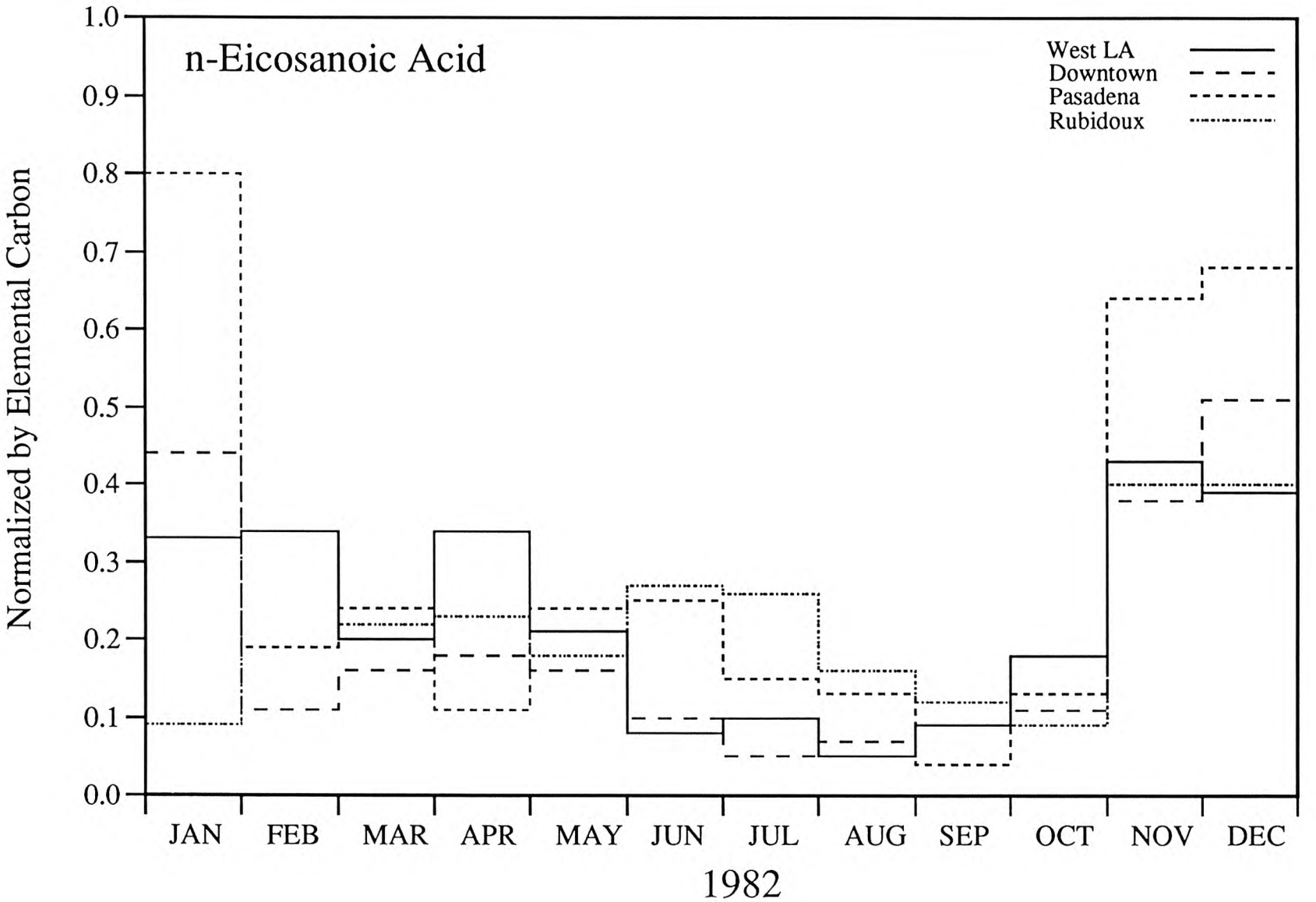
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Eicosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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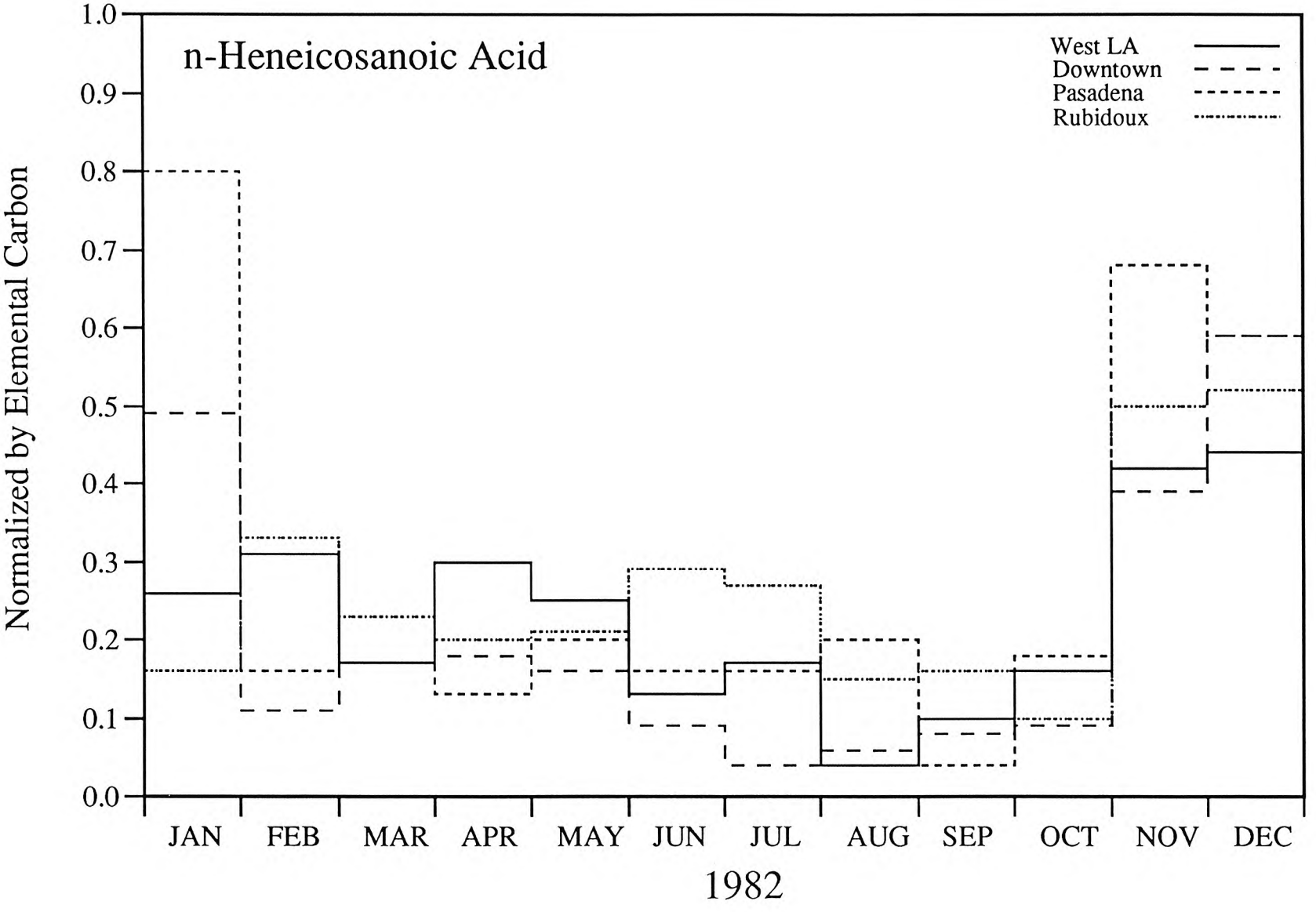
SEP
OCT
NOV
DEC
1982


n-Heneicosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
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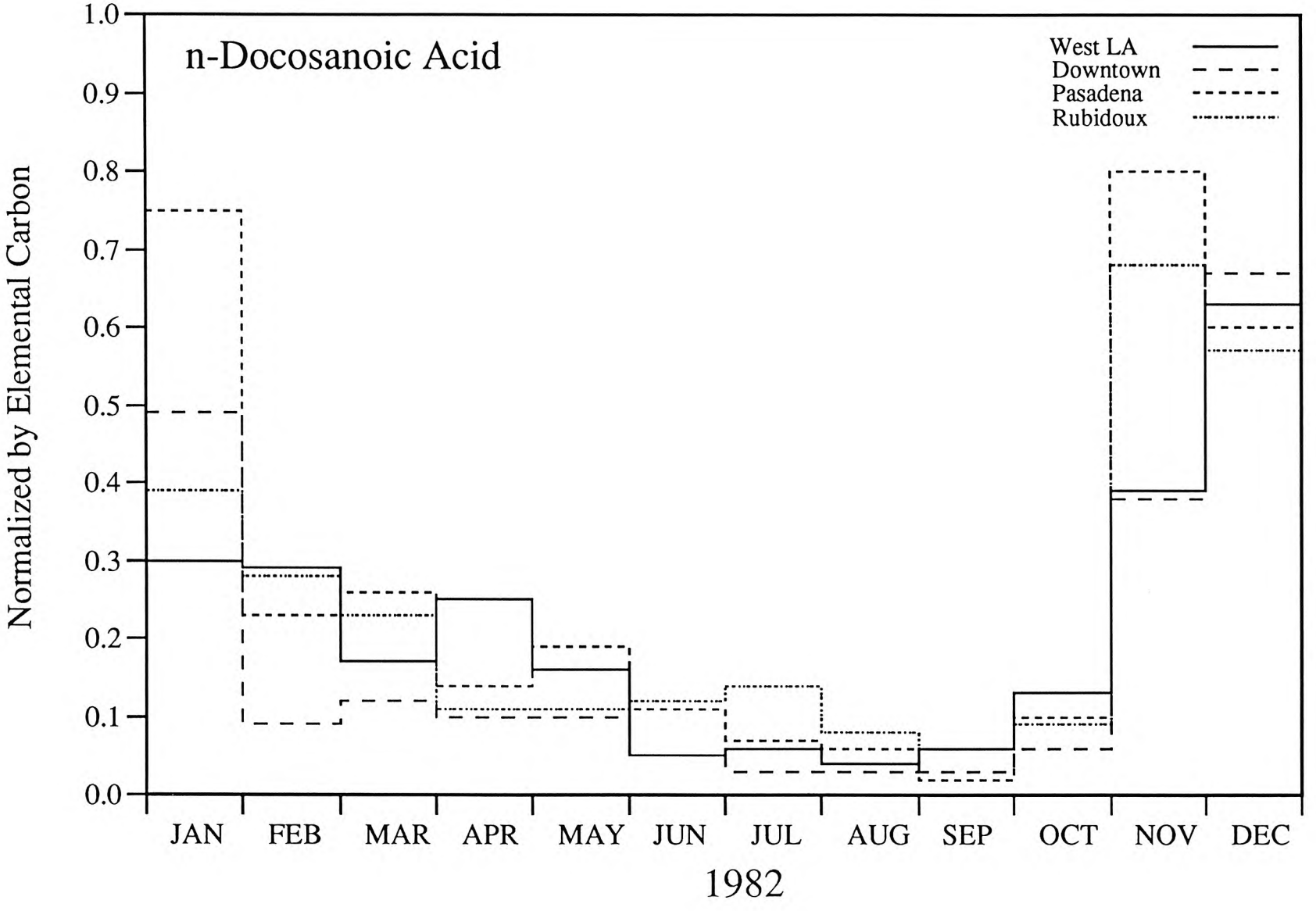
OCT
NOV
DEC
1982


n-Docosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
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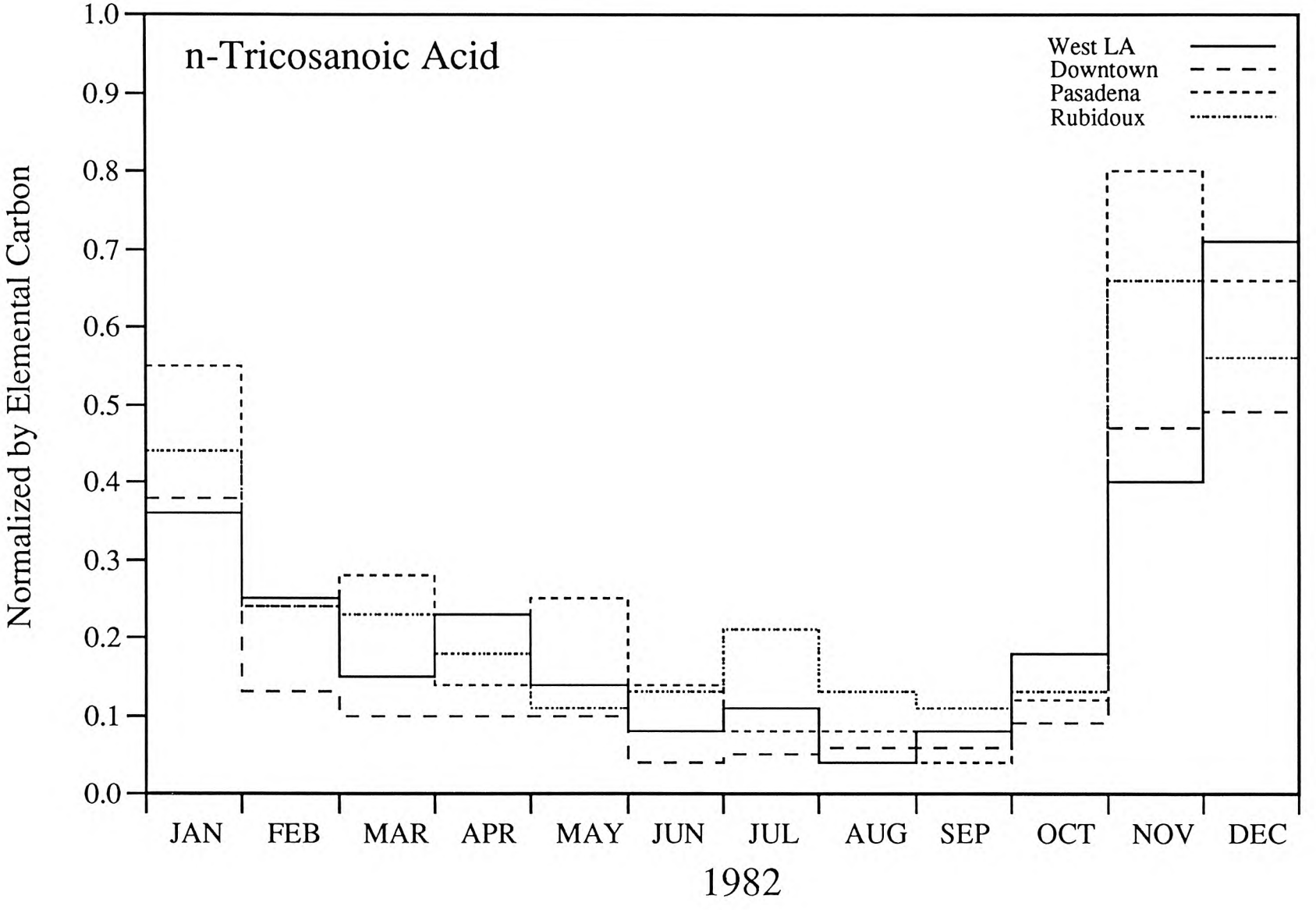
DEC
1982


n-Tricosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
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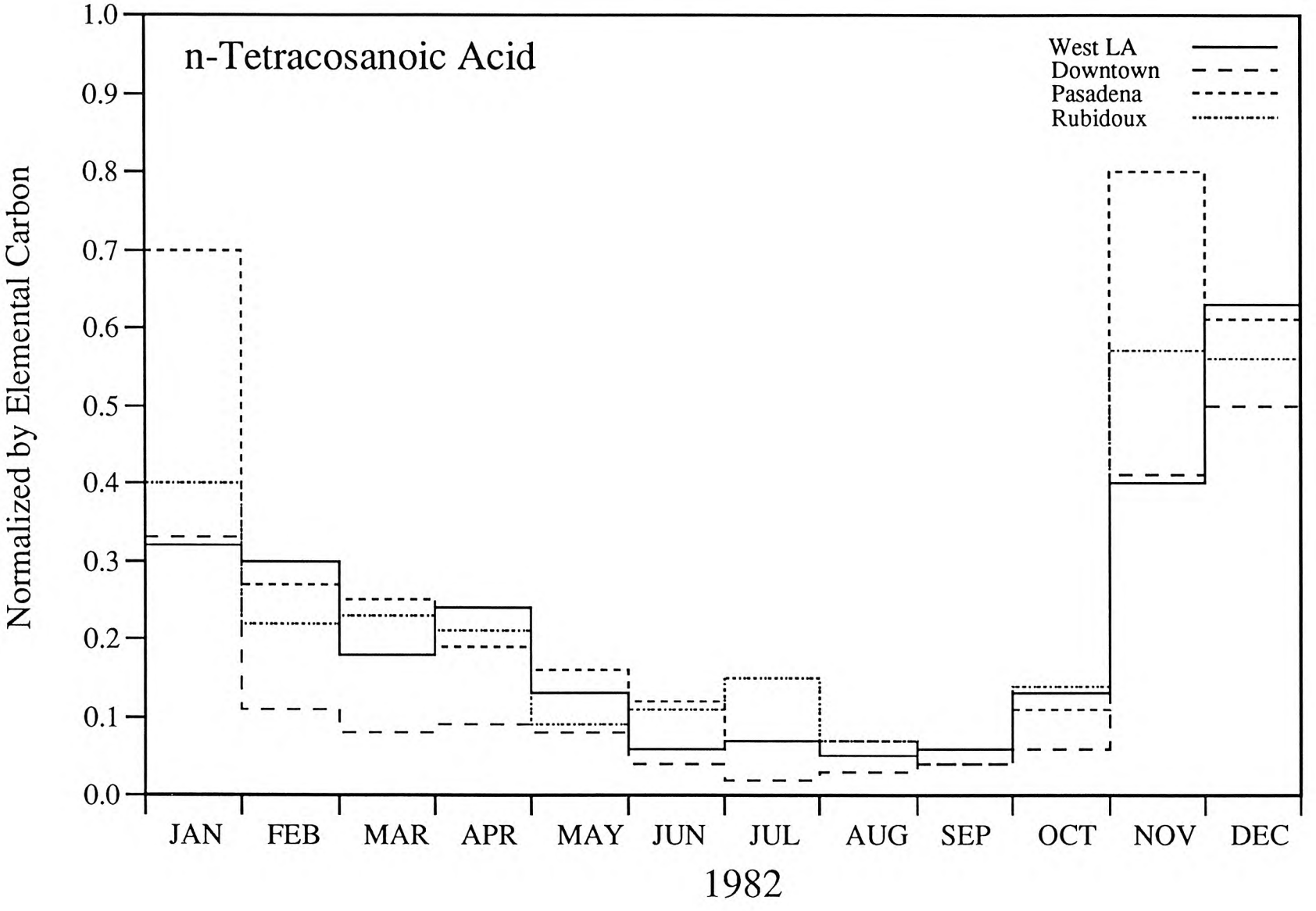
1982


n-Tetracosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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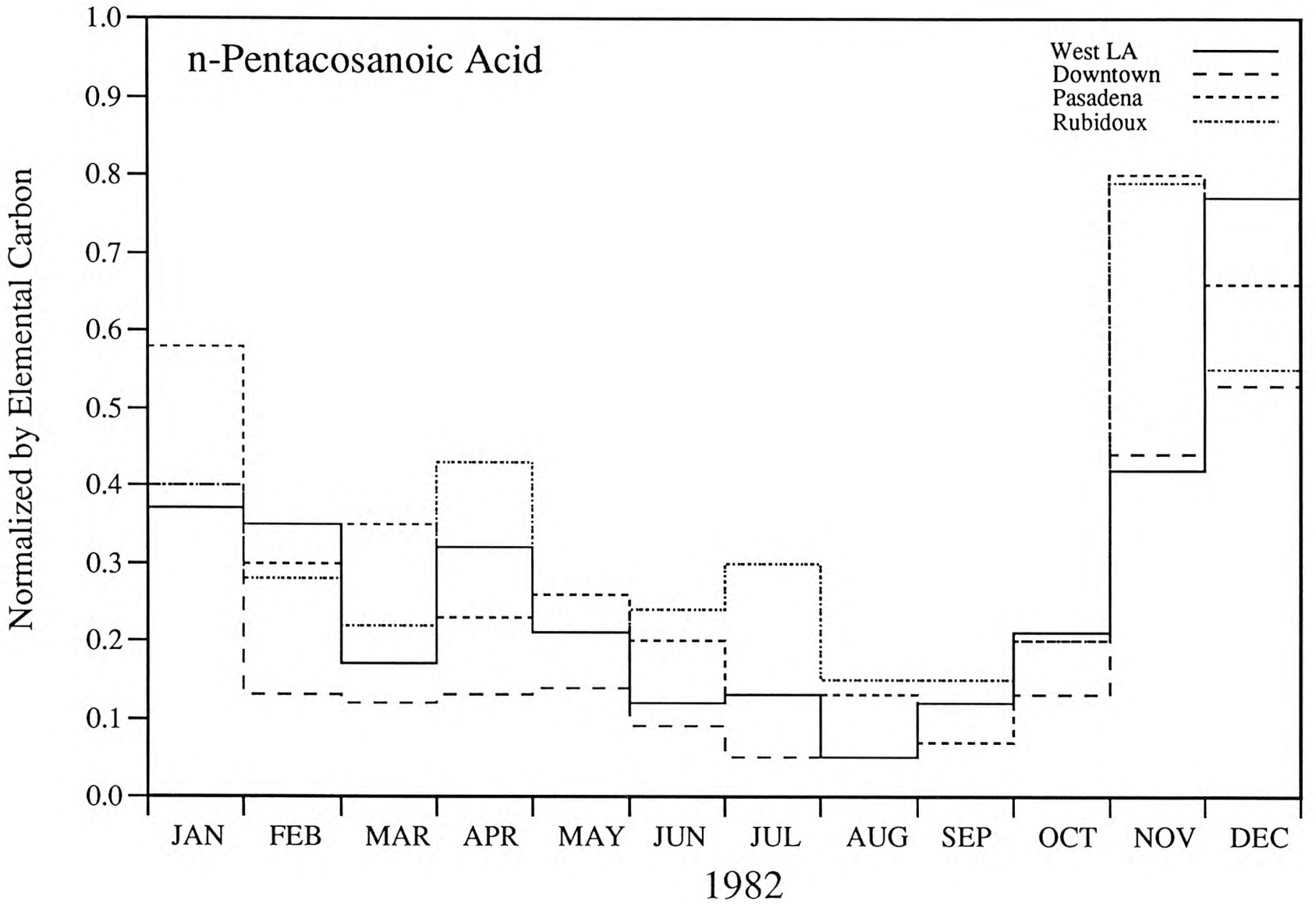
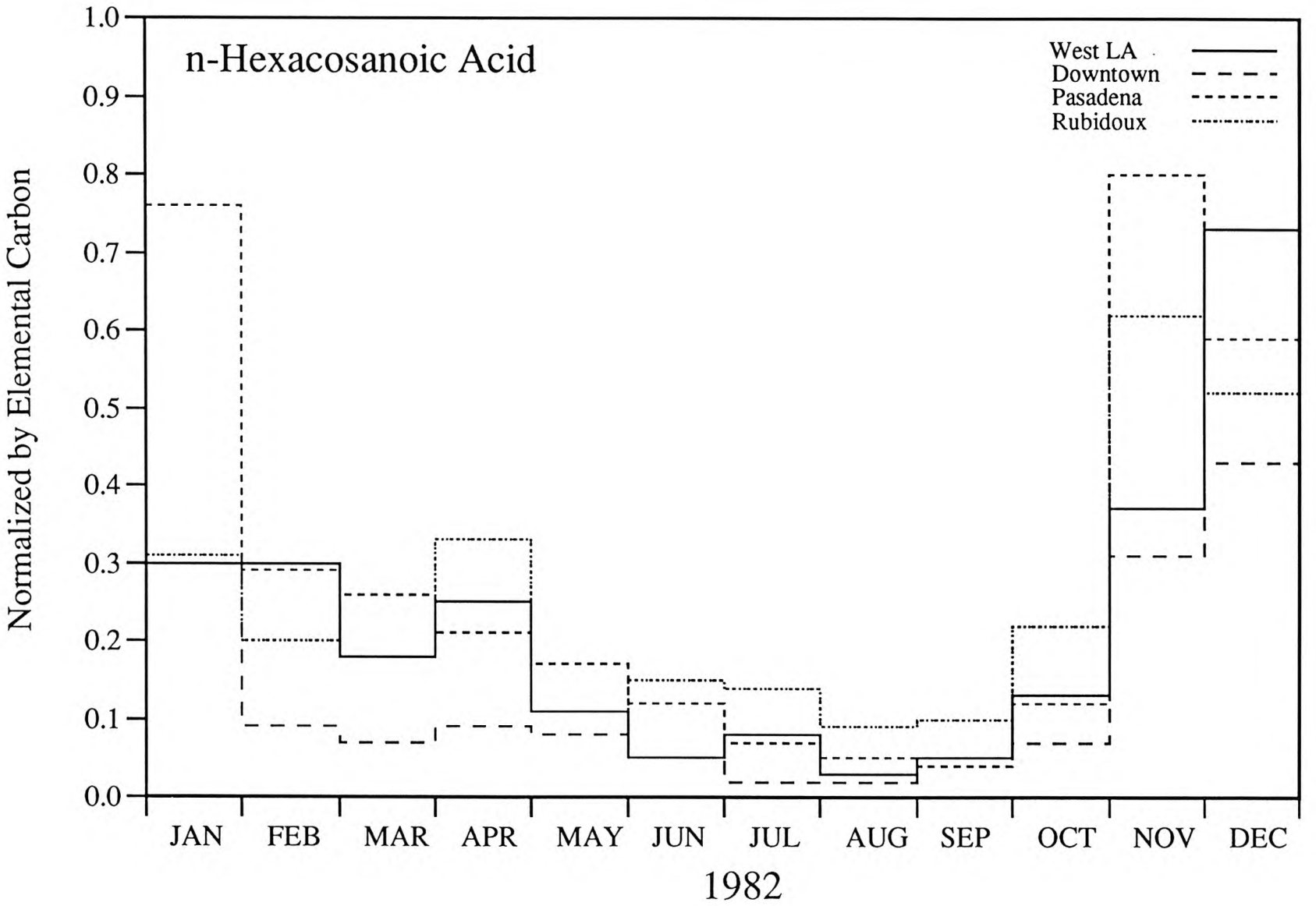
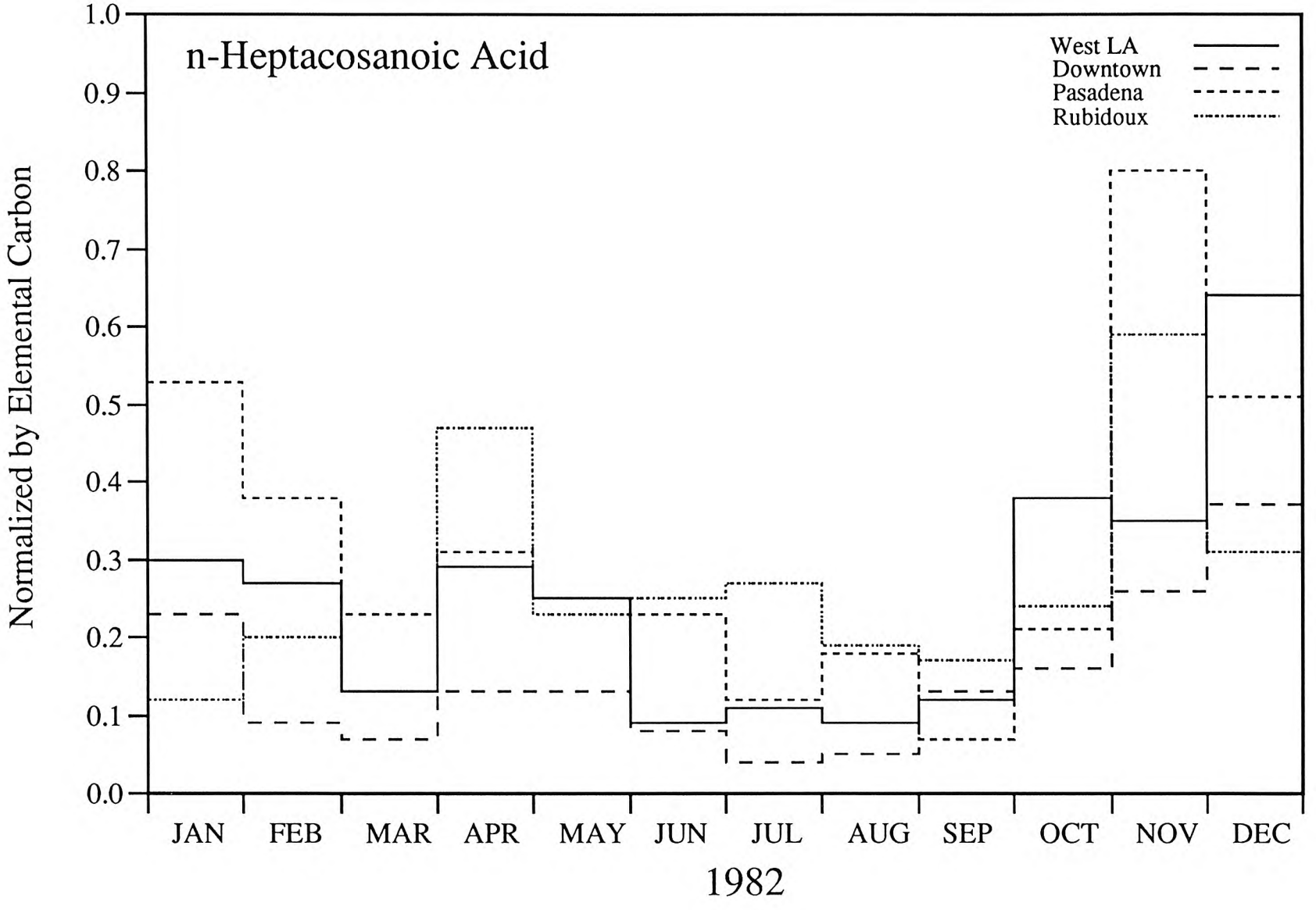
OCT
NOV
DEC
1982


n-Pentacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Hexacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


n-Heptacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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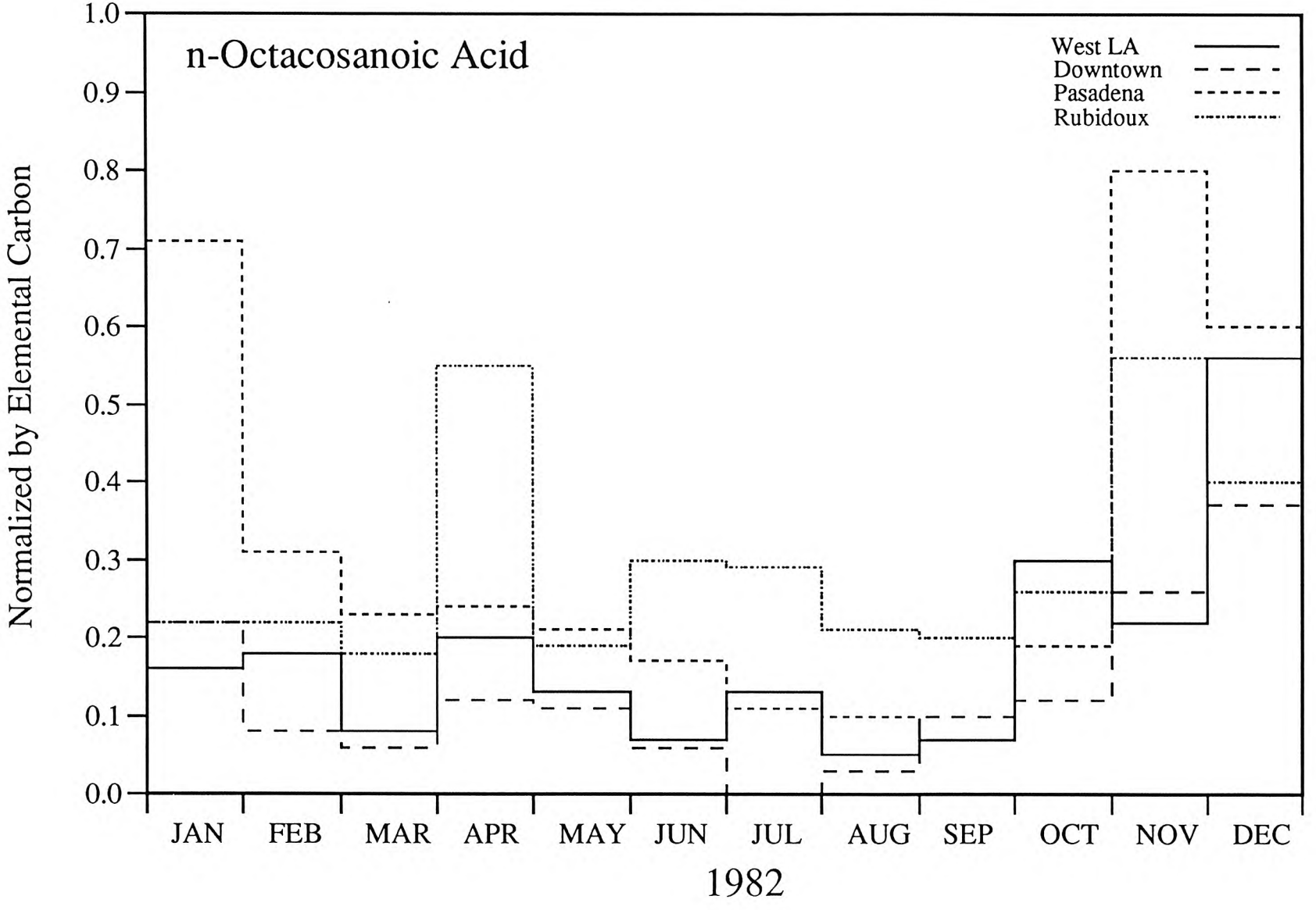
SEP
OCT
NOV
DEC
1982


n-Octacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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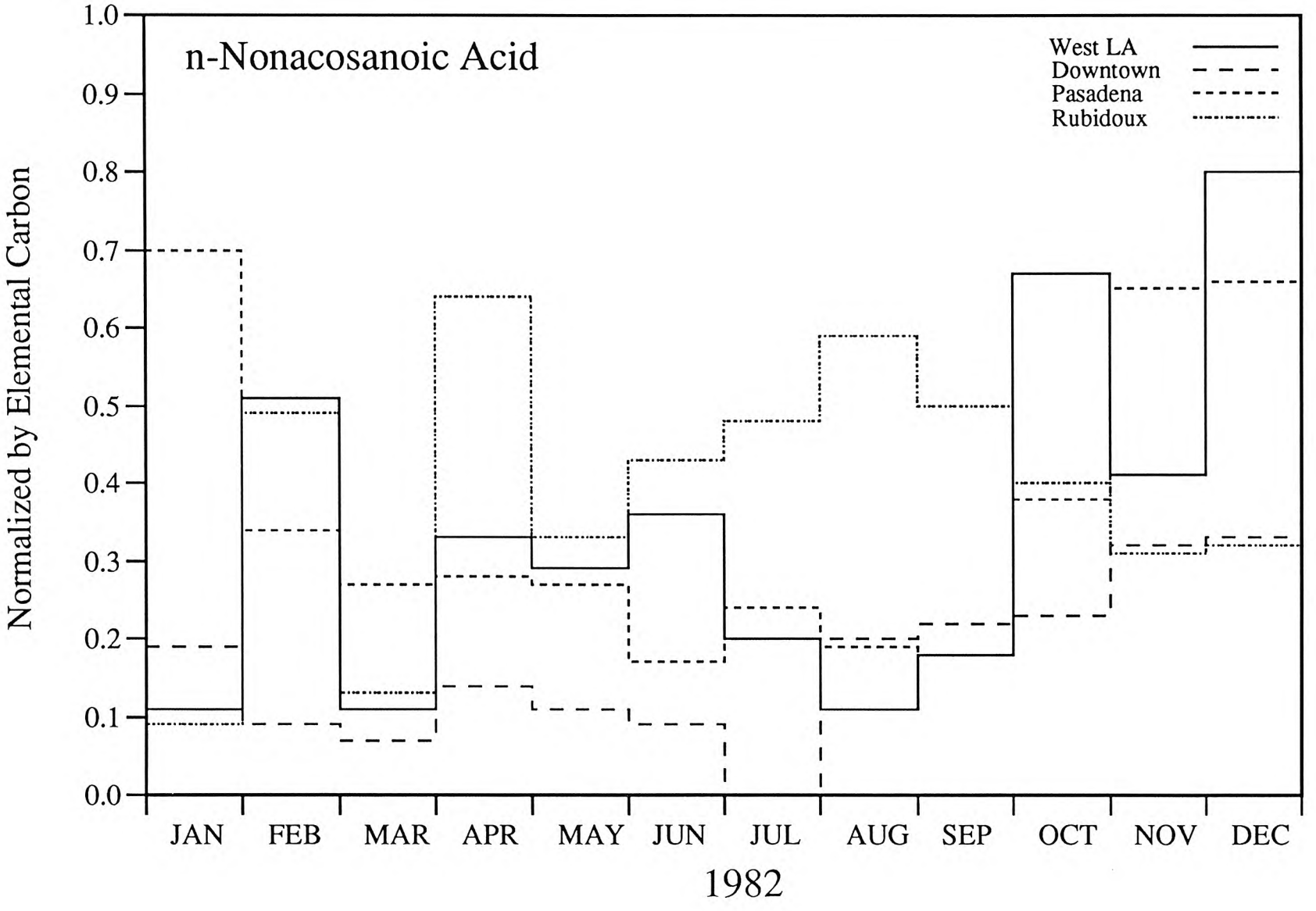
1982


n-Nonacosanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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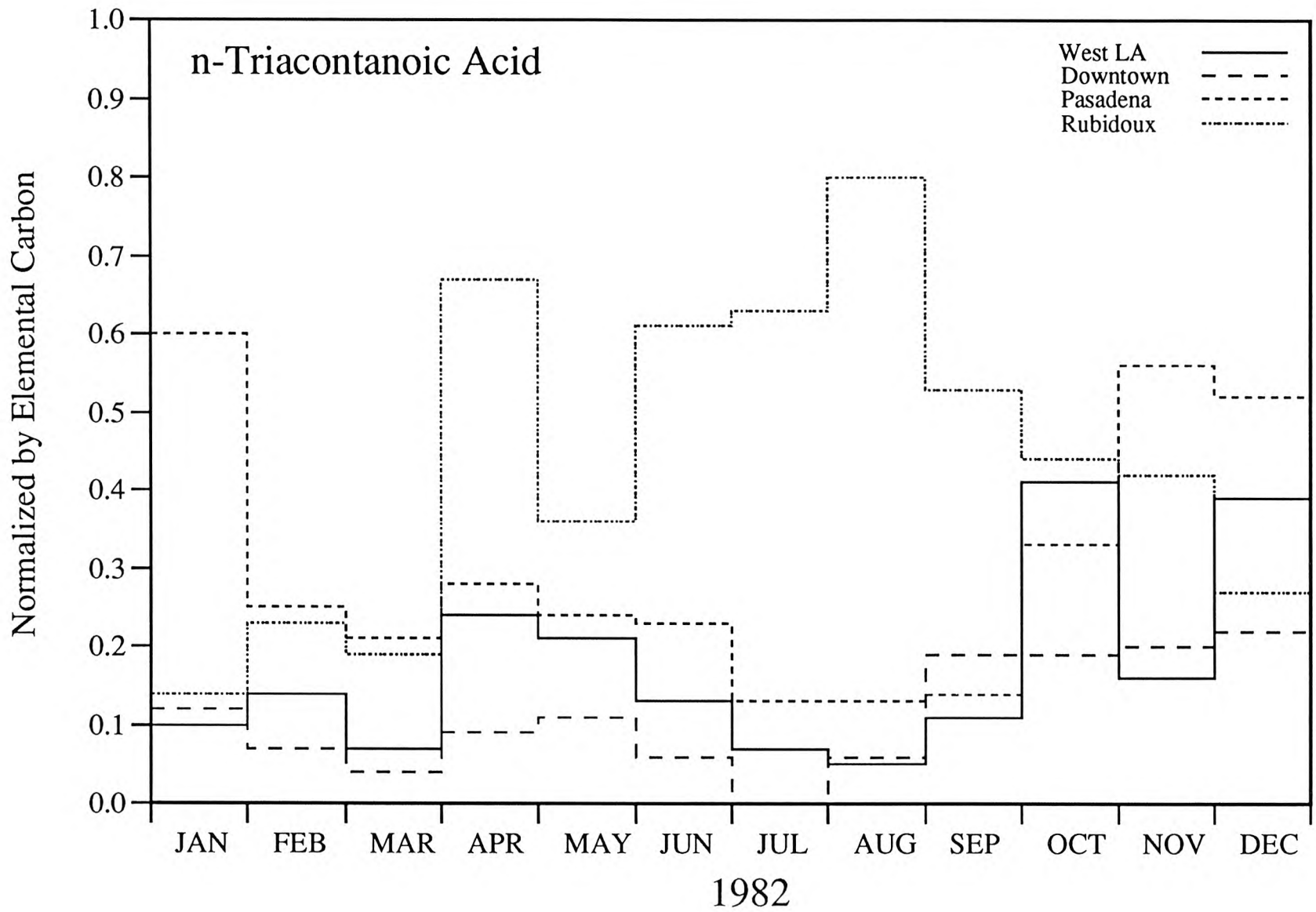
1982


n-Triacontanoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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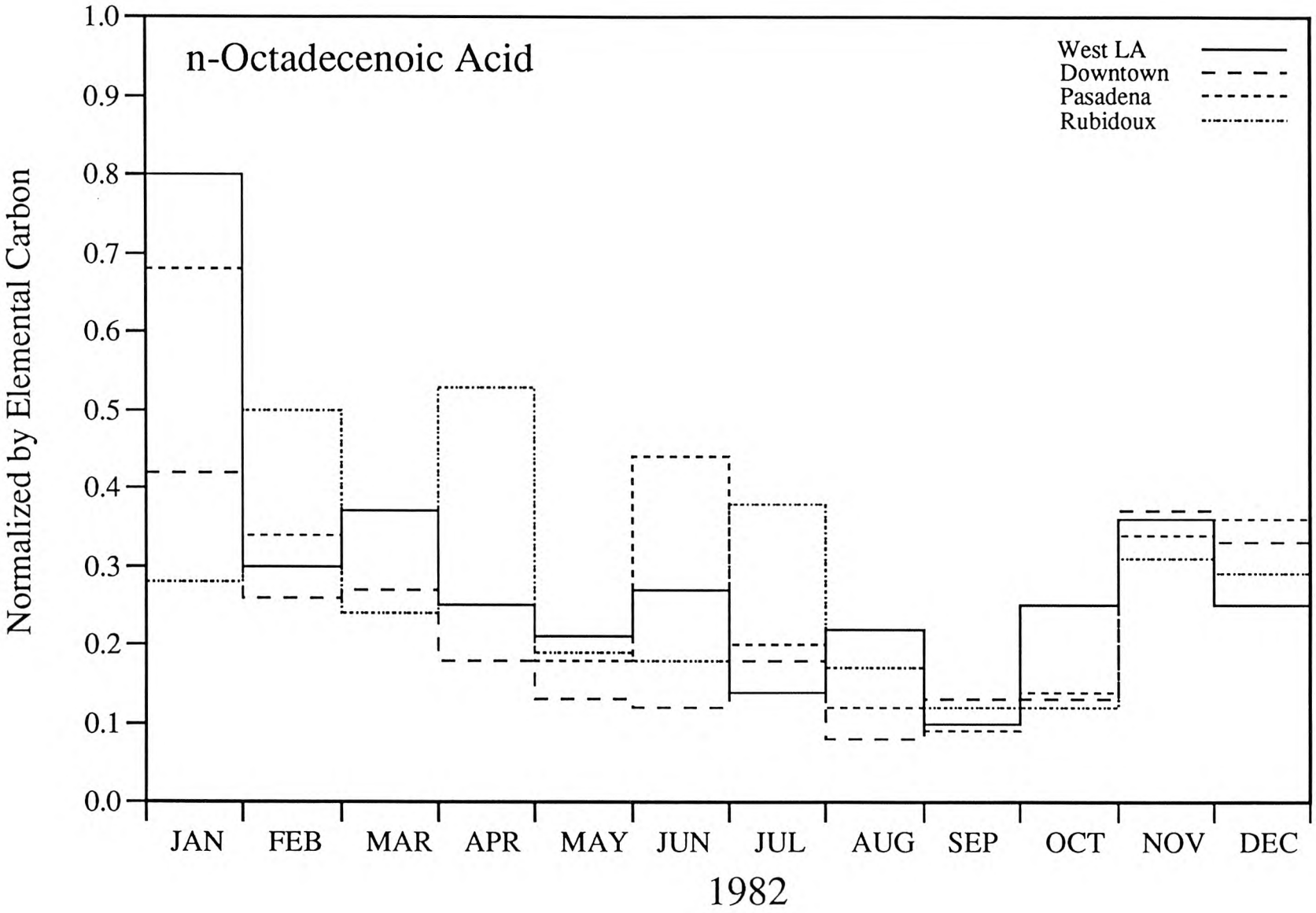
OCT
NOV
DEC
1982

Appendix B3

Normalized Concentration Profiles for n-Alkenoic Acids


n-Octadecenoic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
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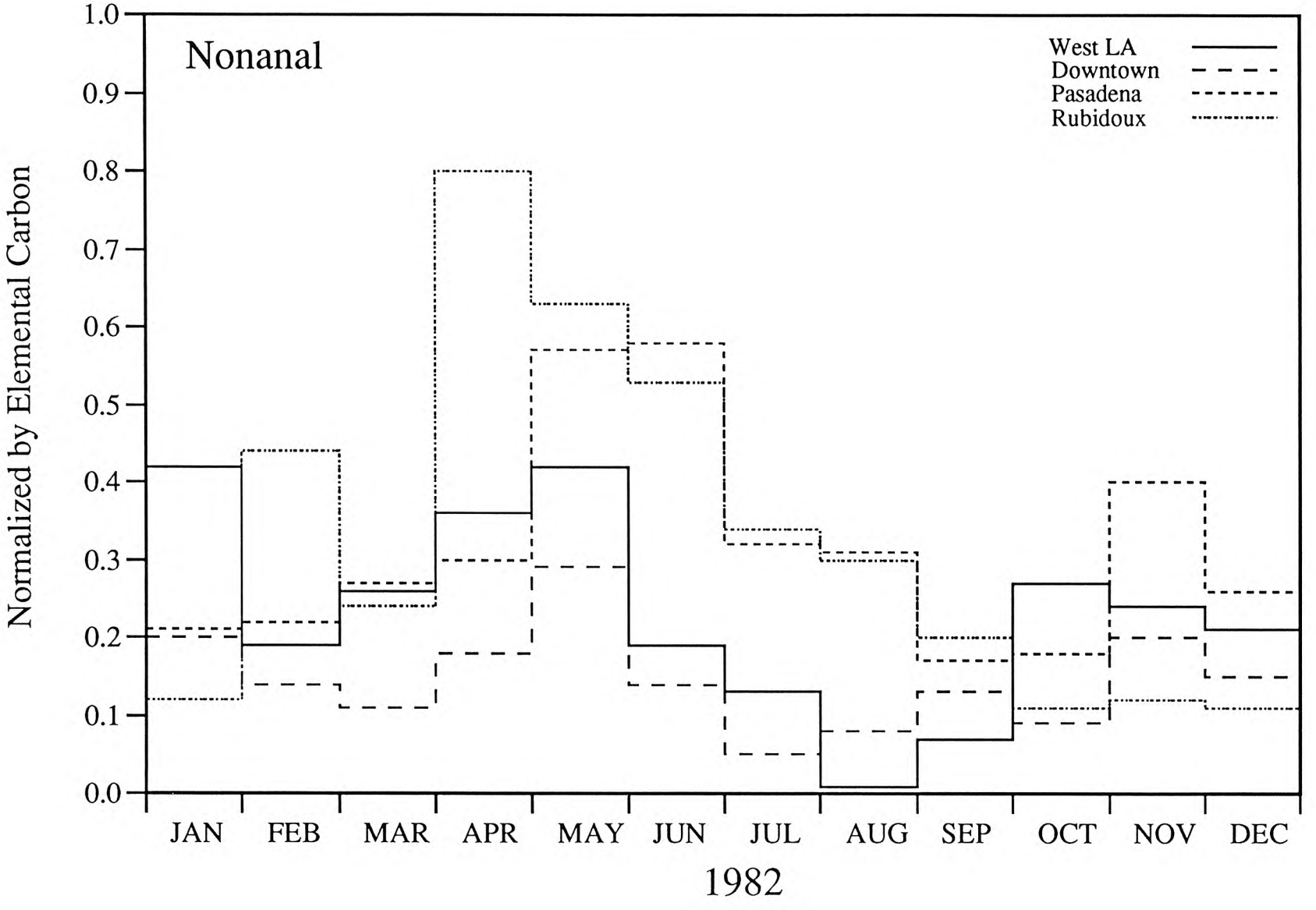
JUL
AUG
SEP
OCT
NOV
DEC
1982

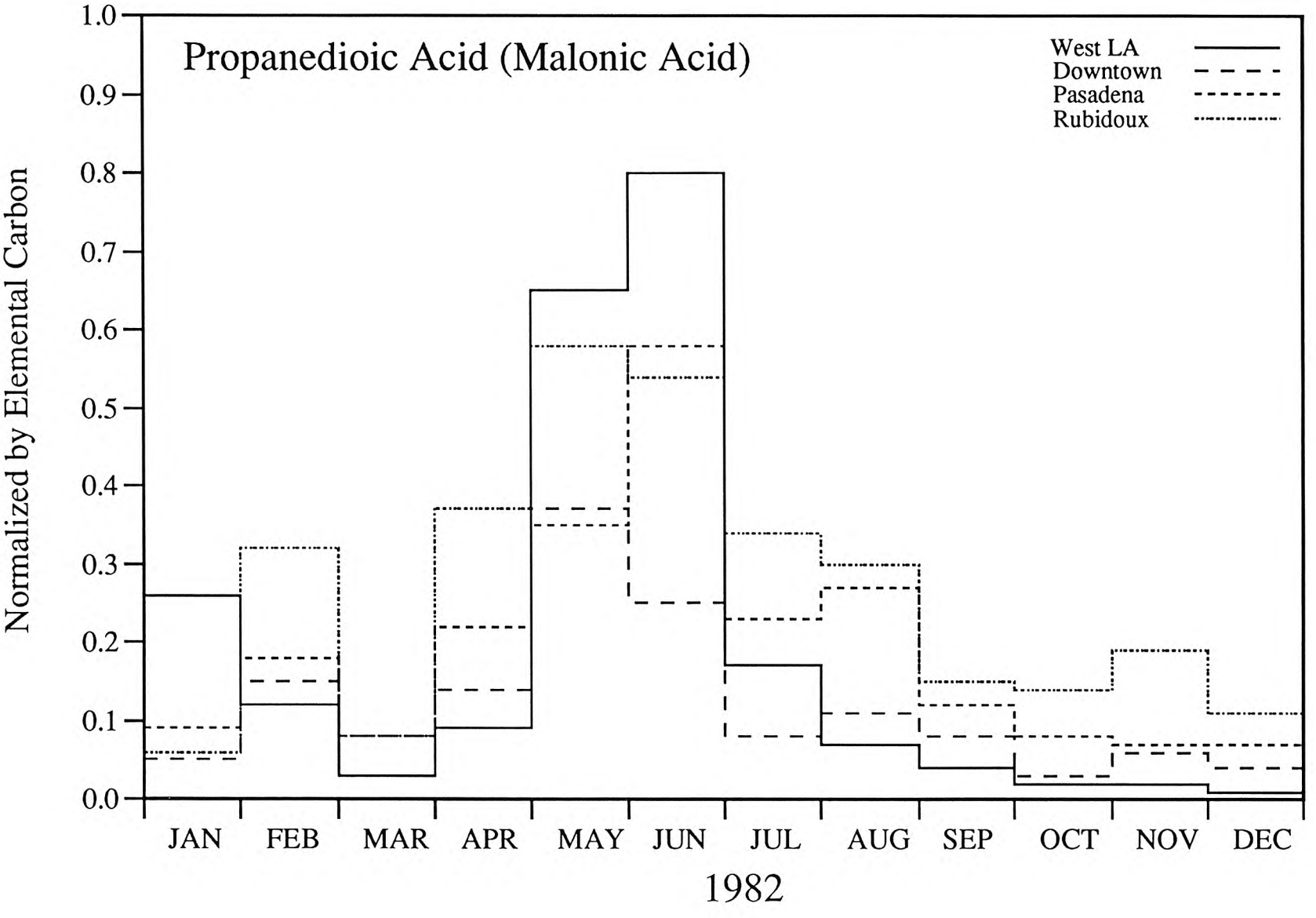
Appendix B4

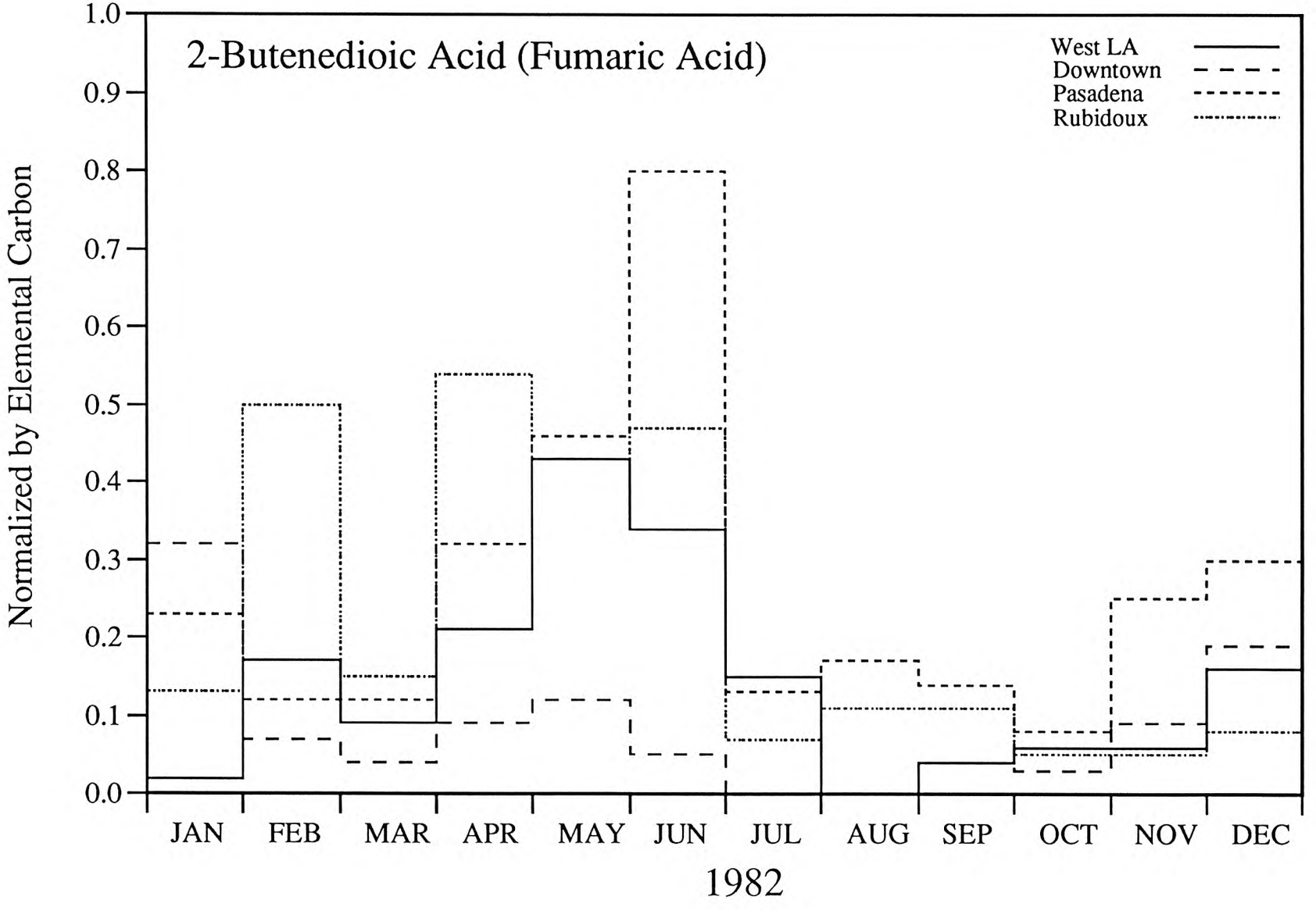
Normalized Concentration Profiles for n-Alkanals


Nonanal
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

Appendix B5

Normalized Concentration Profiles for Aliphatic Dicarboxylic Acids


Propanedioic Acid (Malonic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


2-Butenedioic Acid (Fumaric Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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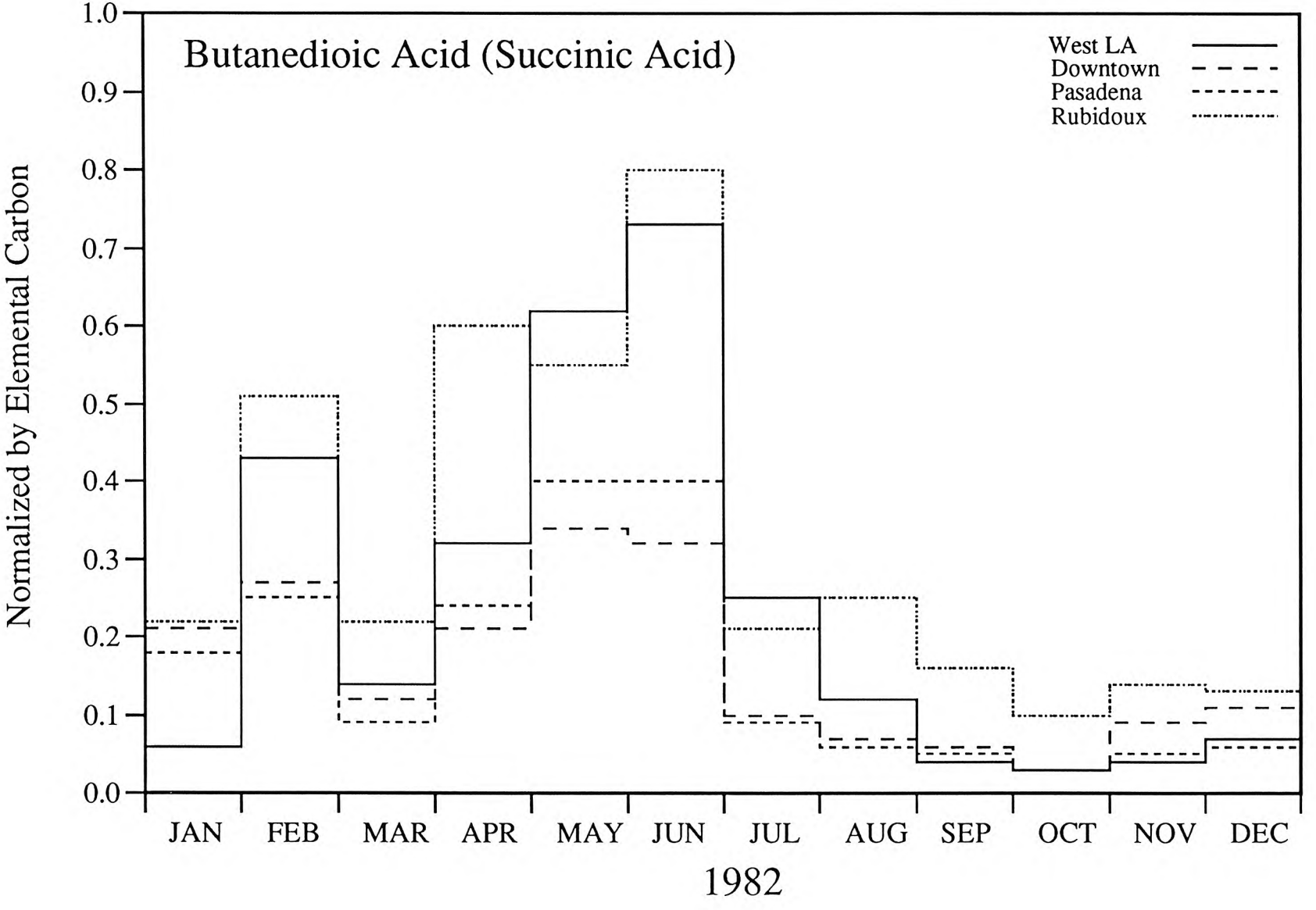
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Butanedioic Acid (Succinic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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JUL
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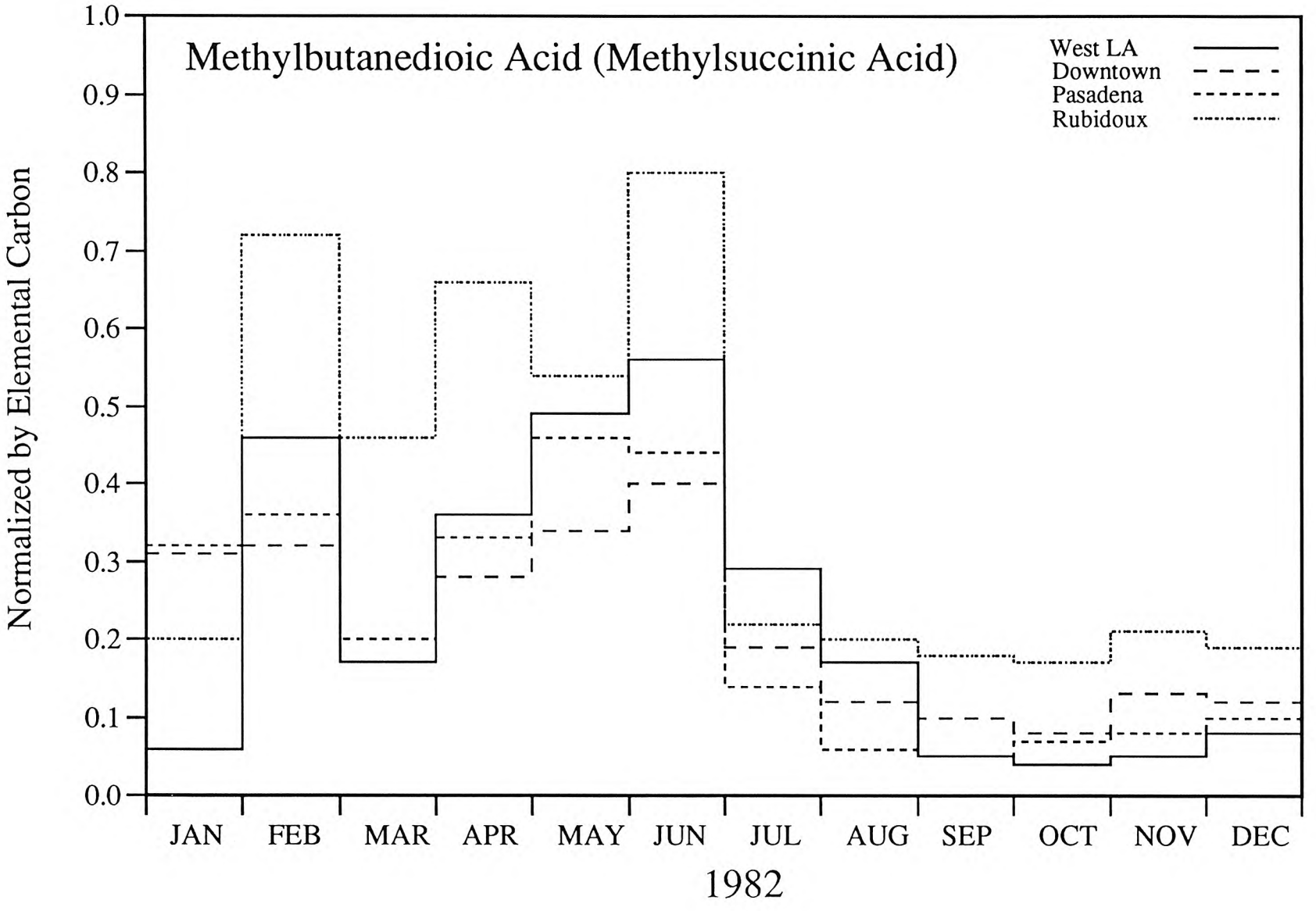
SEP
OCT
NOV
DEC
1982


Methylbutanedioic Acid (Methylsuccinic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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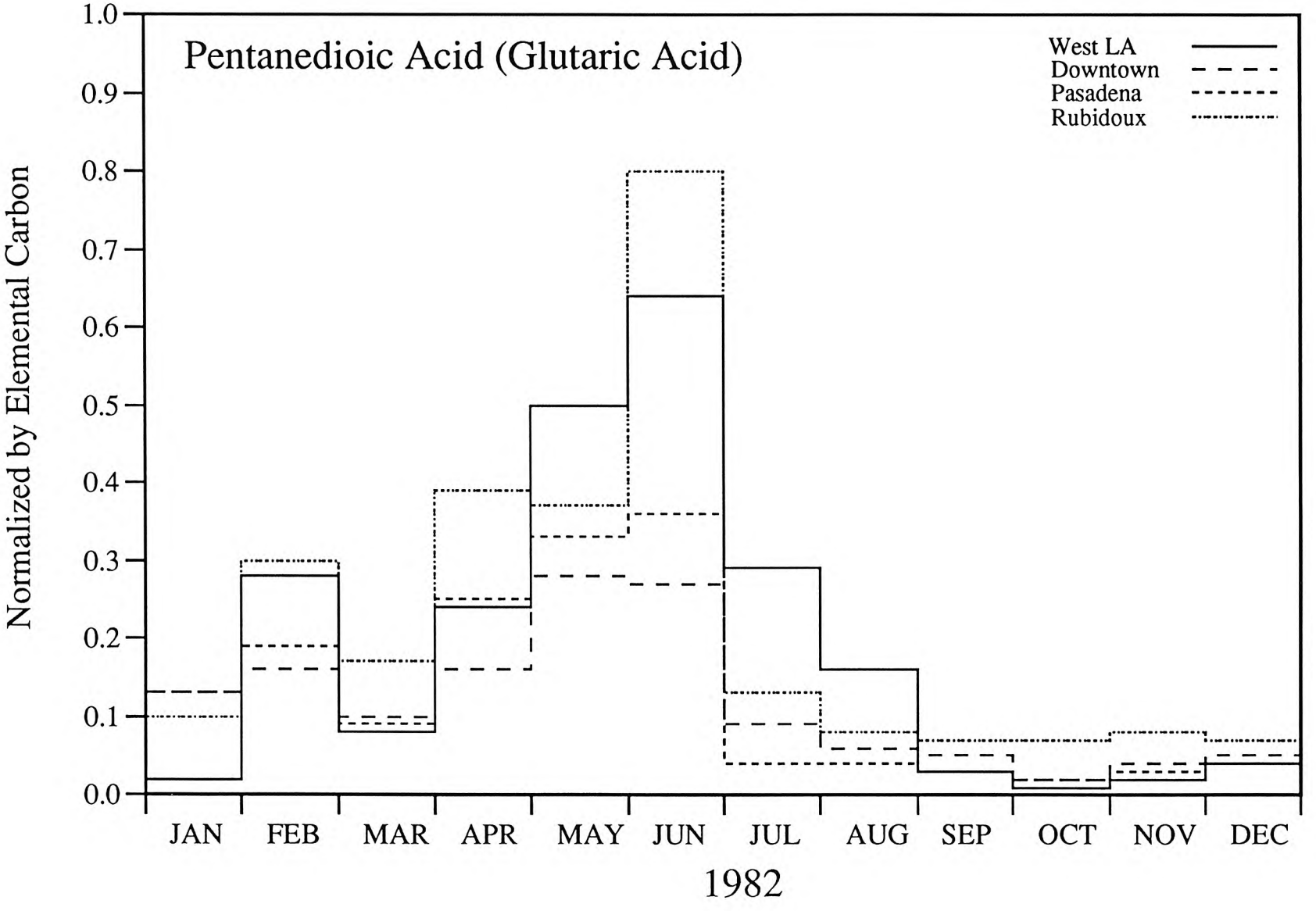
NOV
DEC
1982


Pentanedioic Acid (Glutaric Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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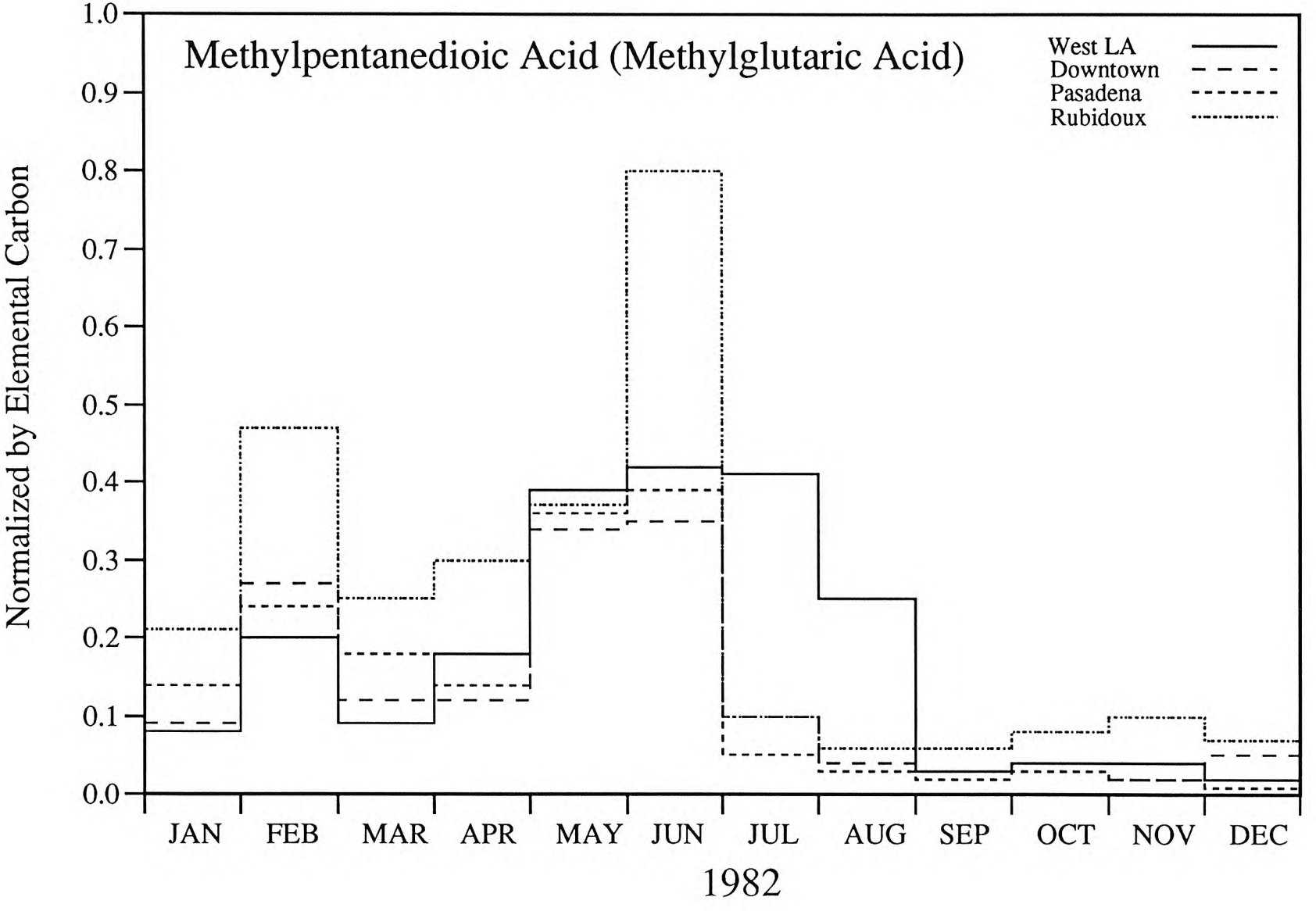
NOV
DEC
1982


Methylpentanedioic Acid (Methylglutaric Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
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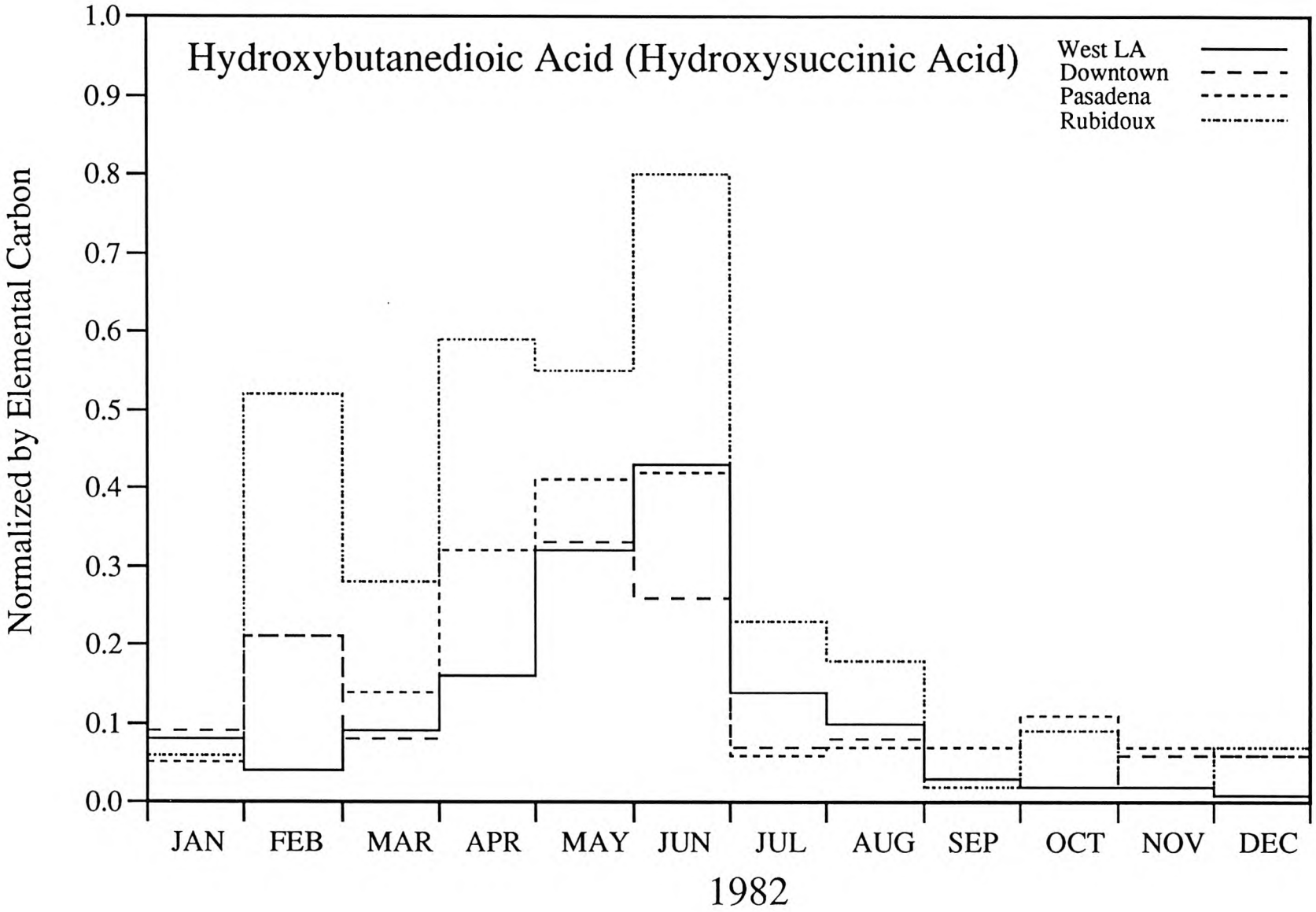
1982


Hydroxybutanedioic Acid (Hydroxysuccinic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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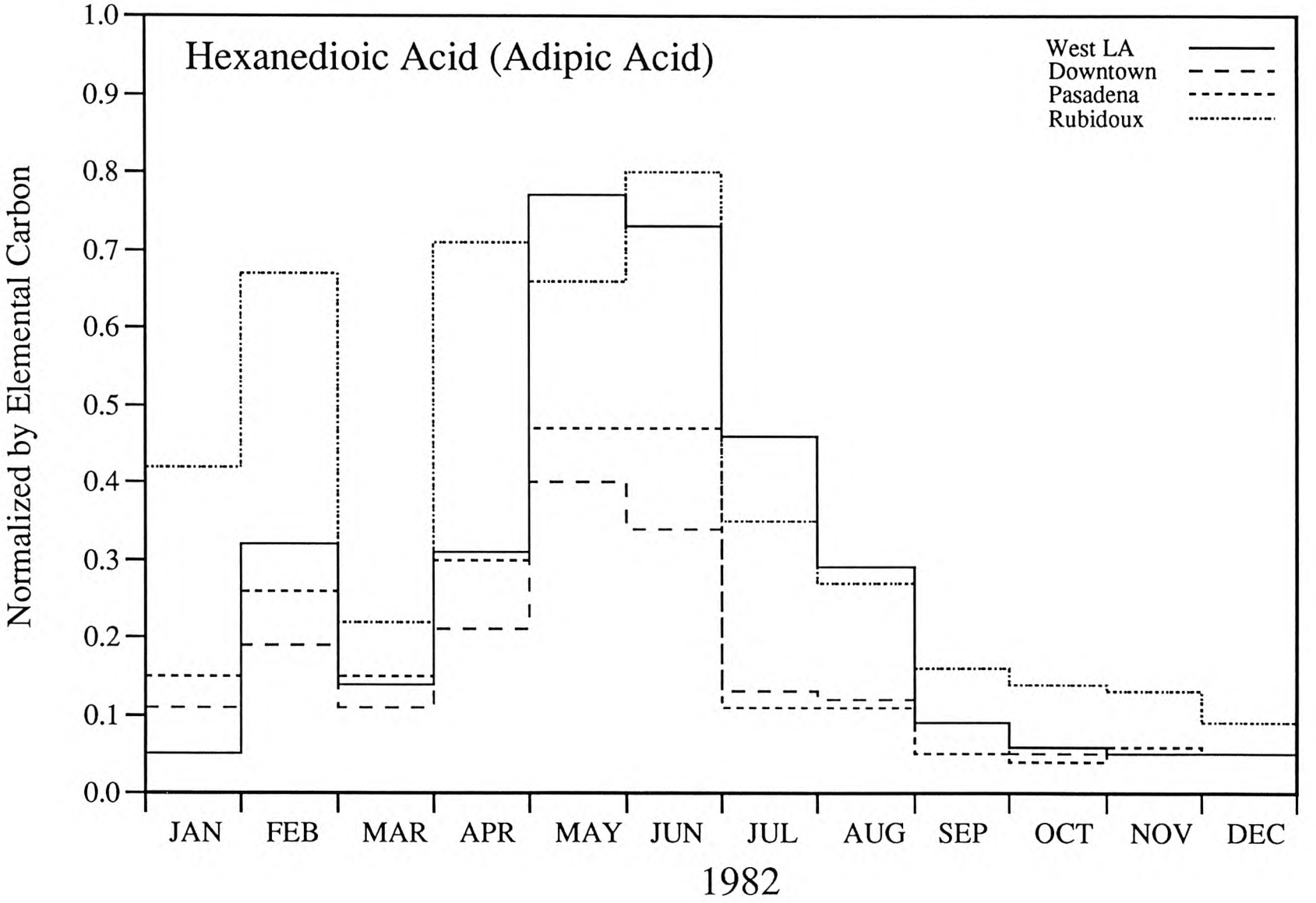
DEC
1982


Hexanedioic Acid (Adipic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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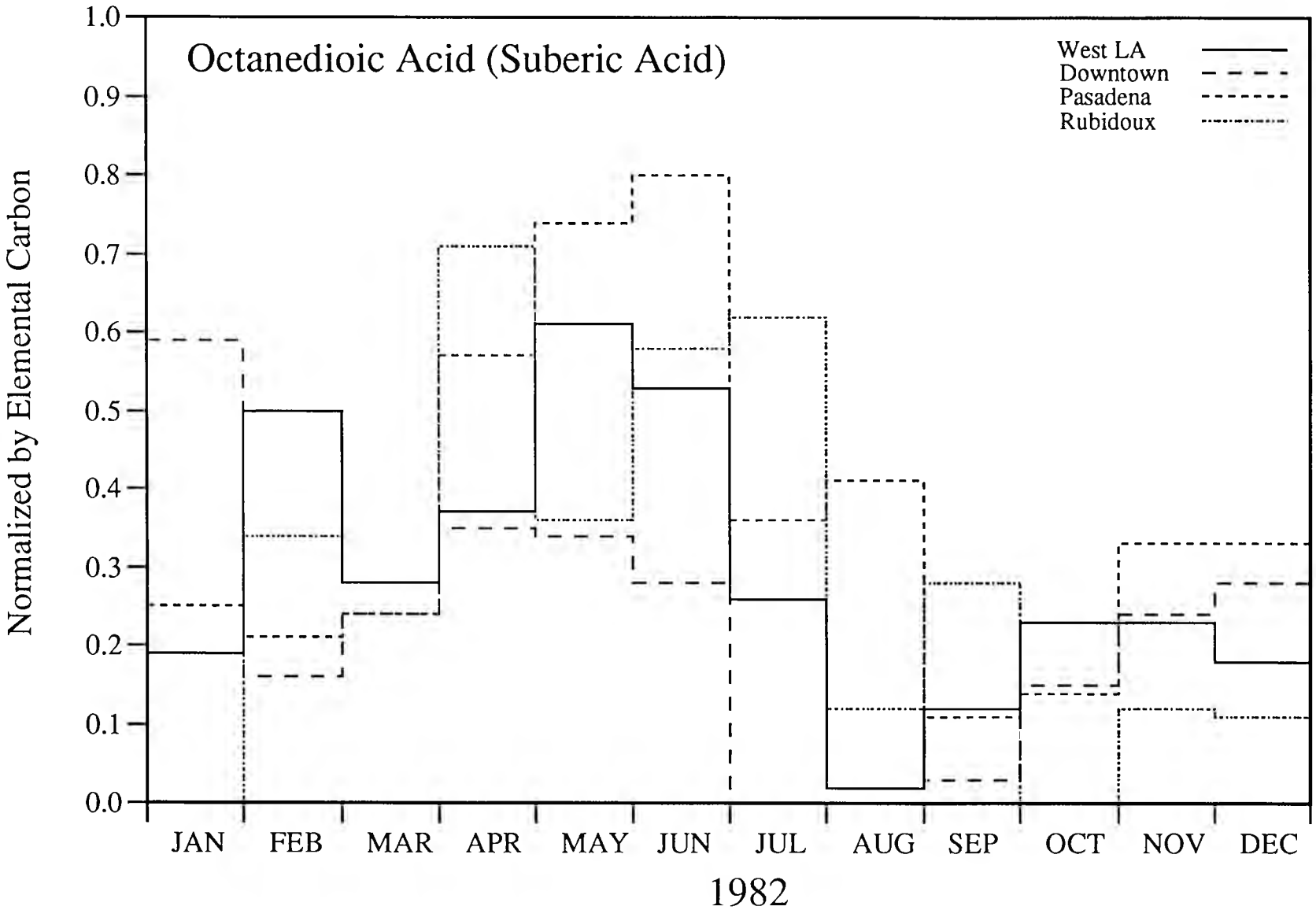
NOV
DEC
1982


Octanedioic Acid (Suberic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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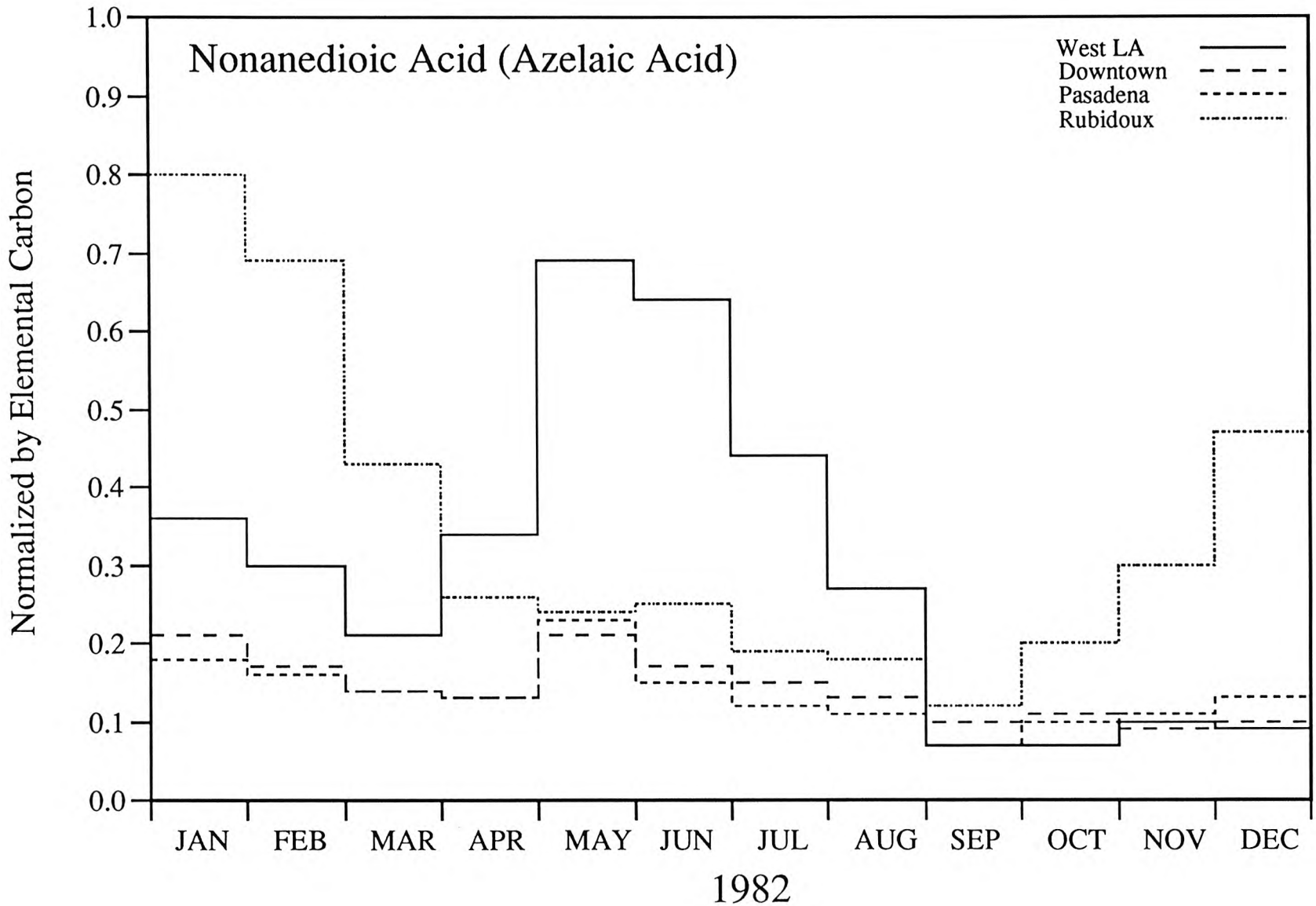
Nonanedioic Acid (Azelaic Acid)
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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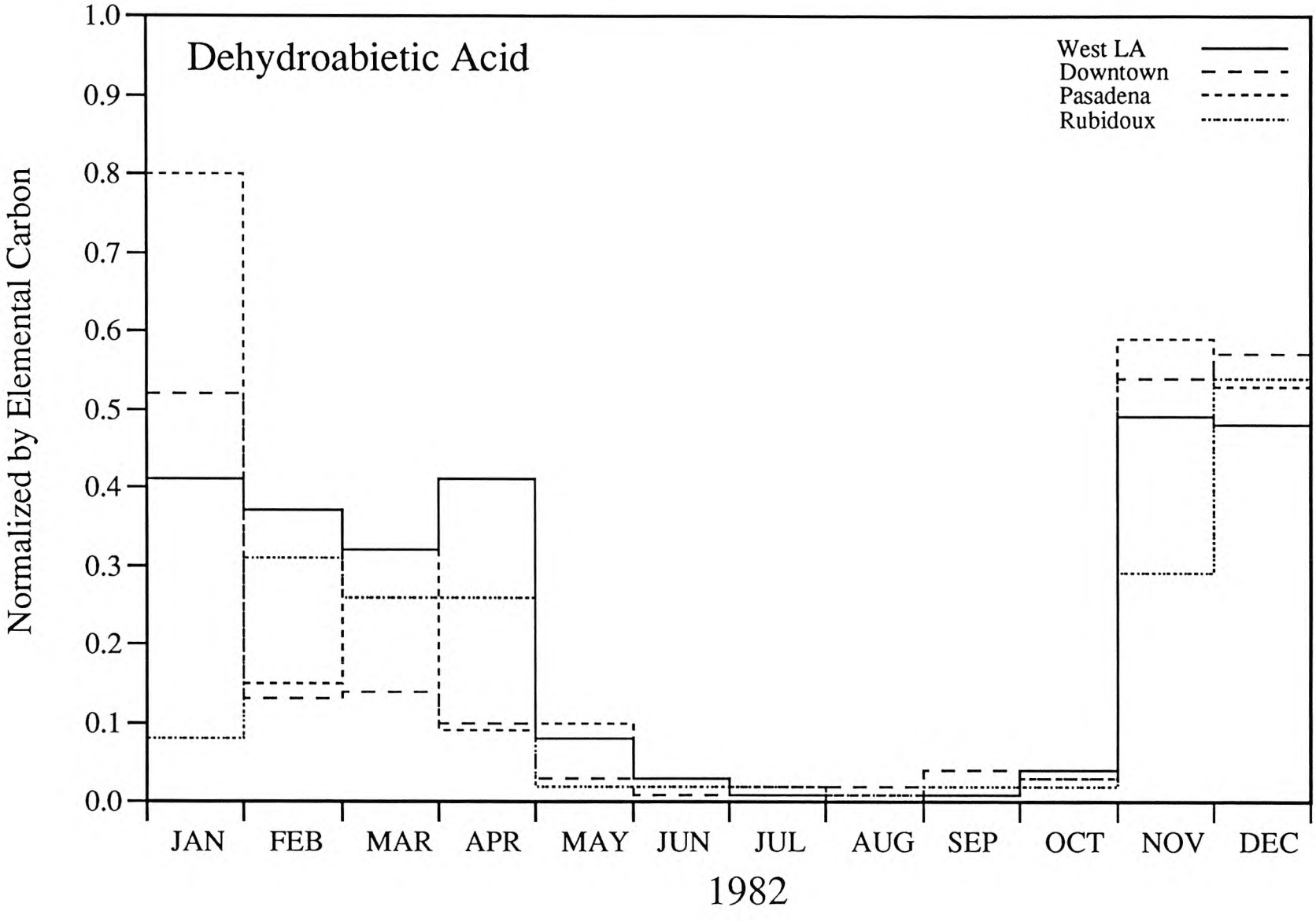
1982

Appendix B6

Normalized Concentration Profiles for Diterpenoid Acids and Retene


Dehydroabietic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
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JUL
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NOV
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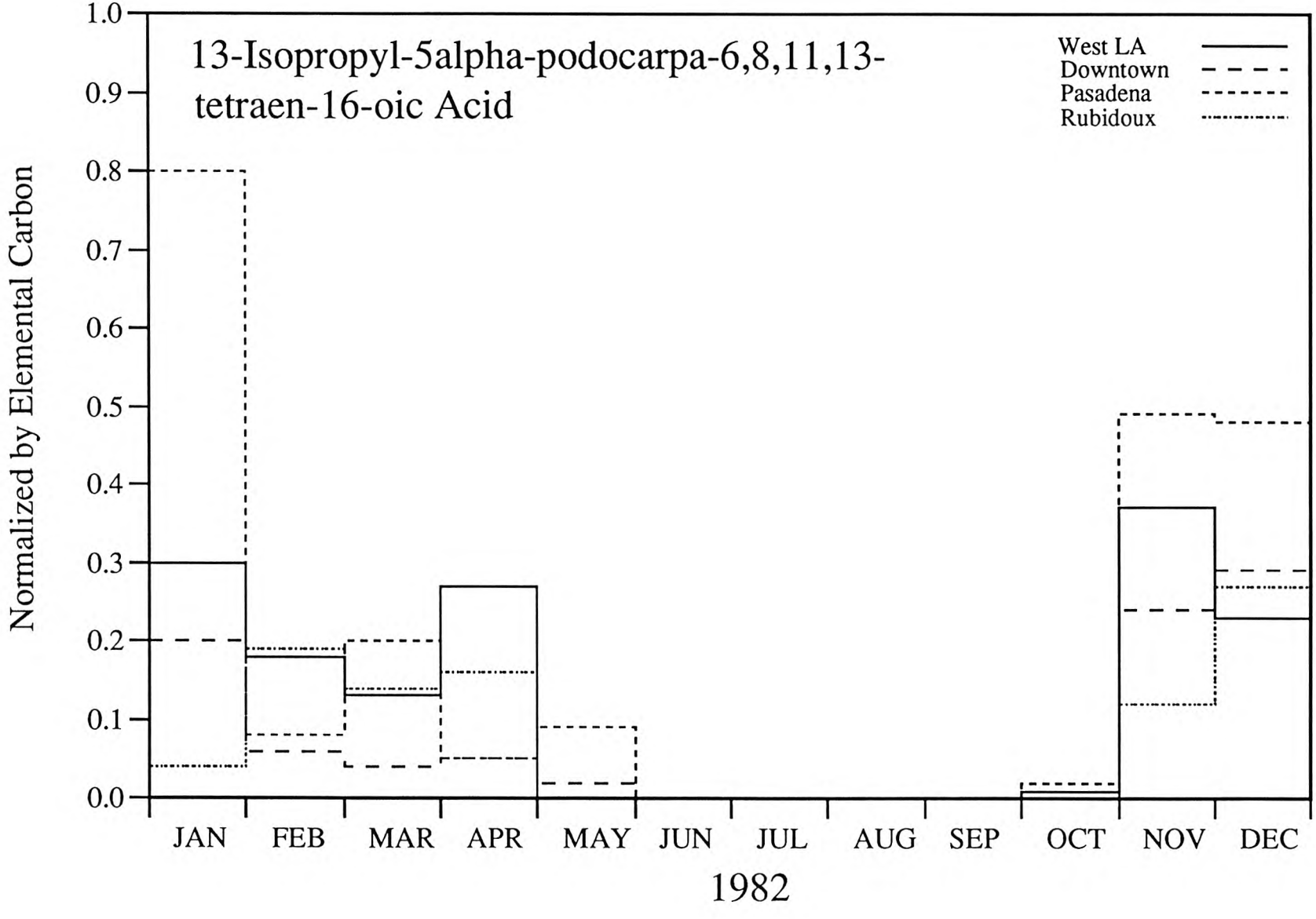
1982


13-Isopropyl-5alpha-podocarpa-6,8,11,13-tetraen-16-oic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
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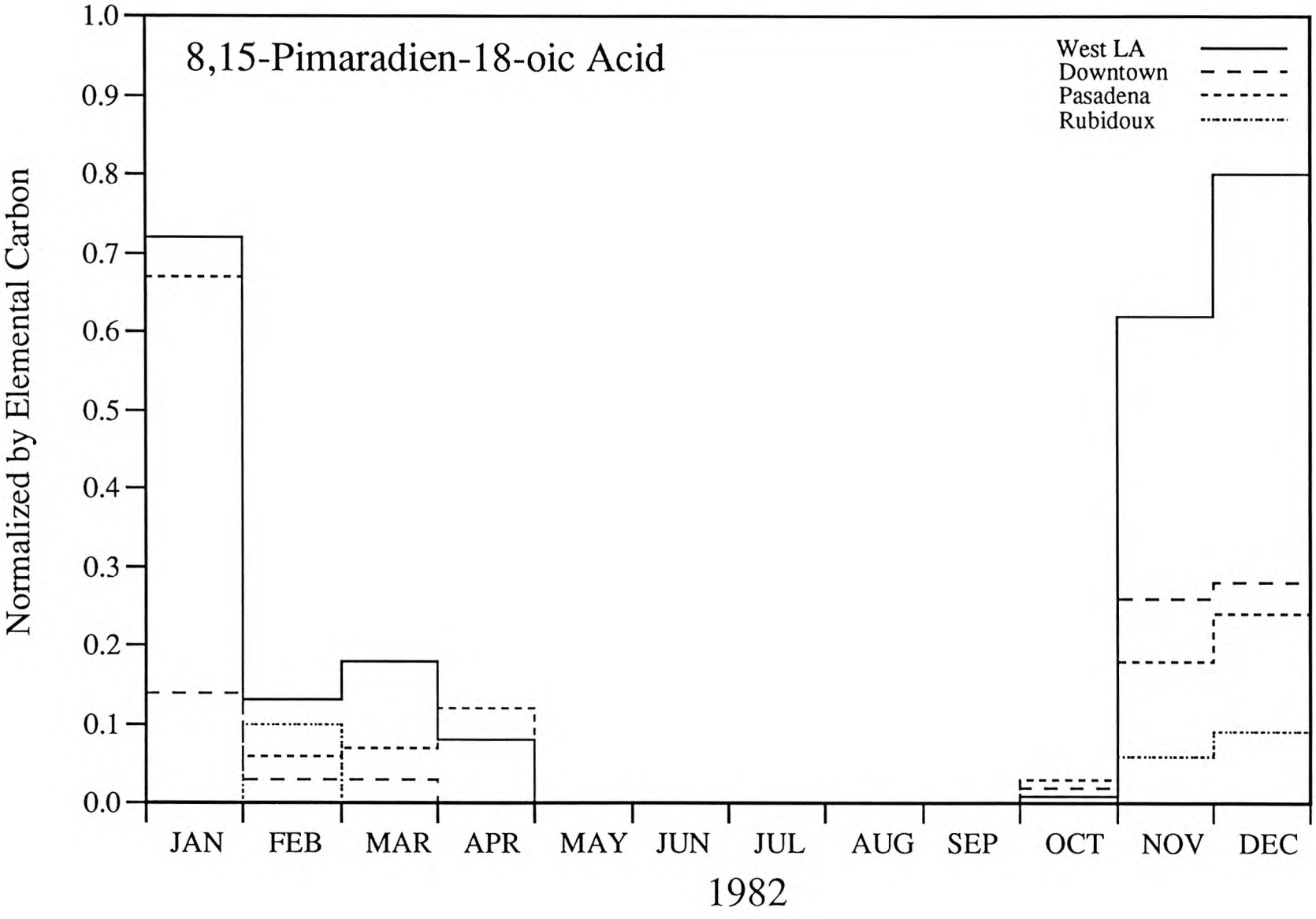
1982


8,15-Pimaradien-18-oic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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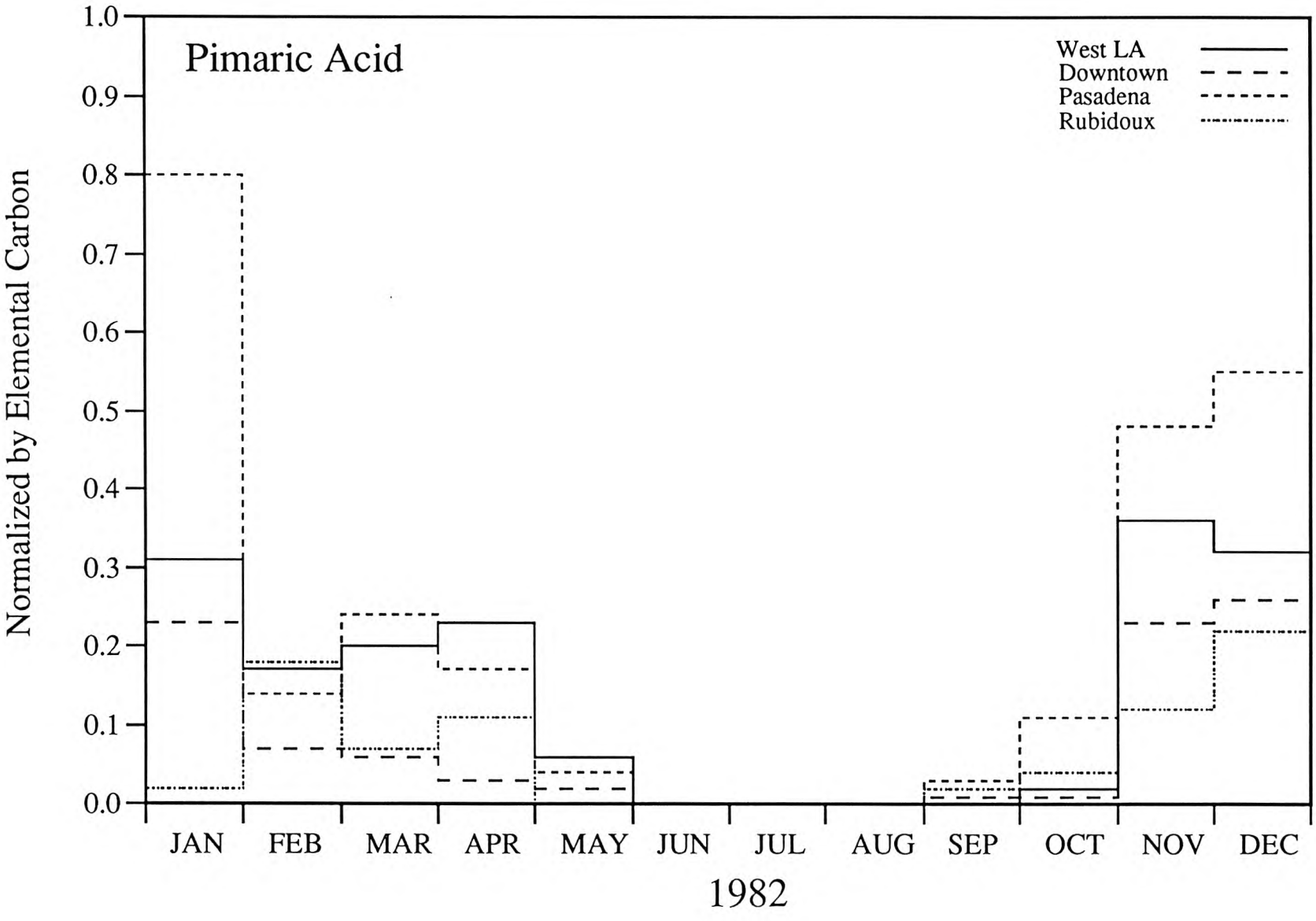
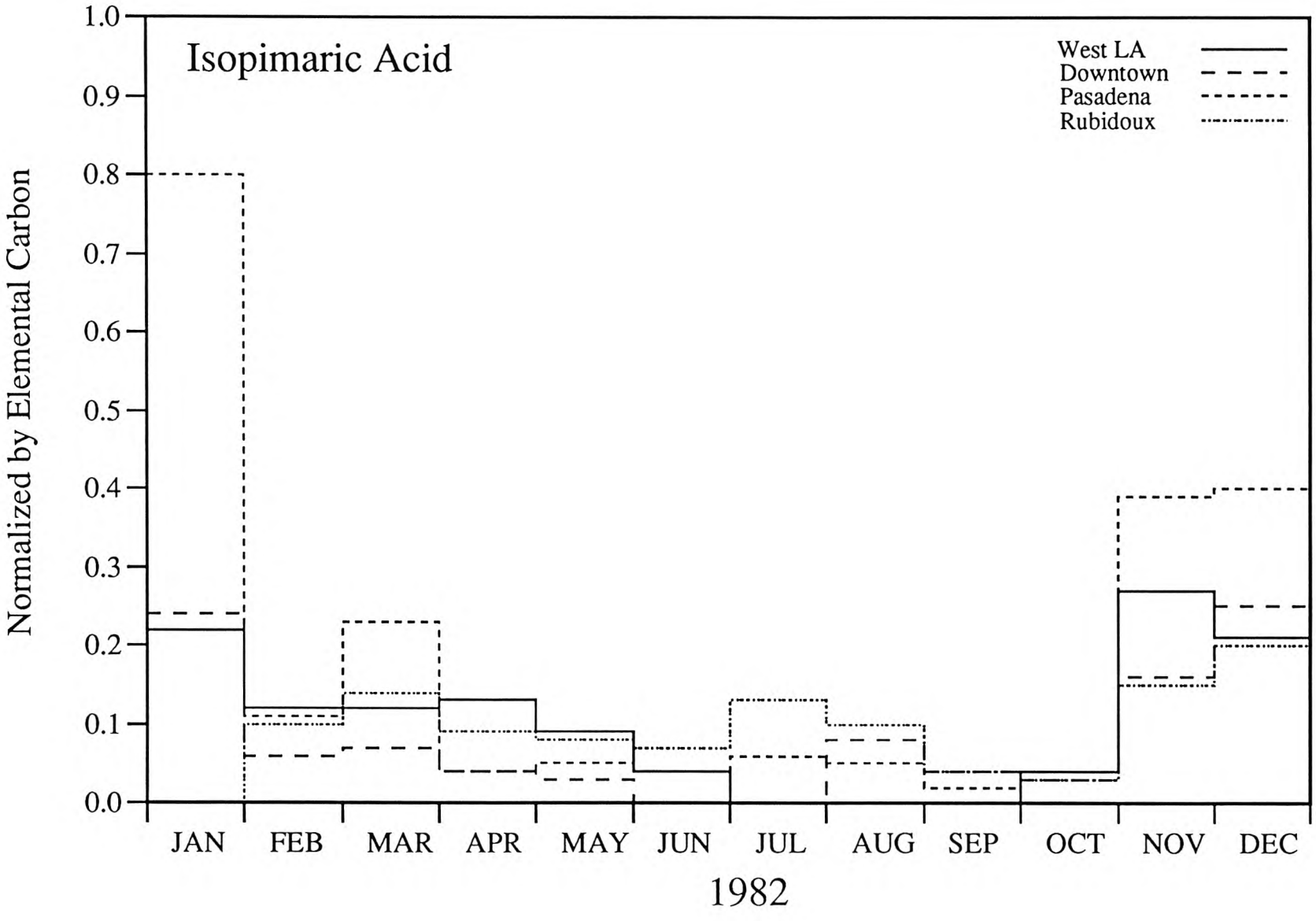
DEC
1982


Pimaric Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Isopimaric Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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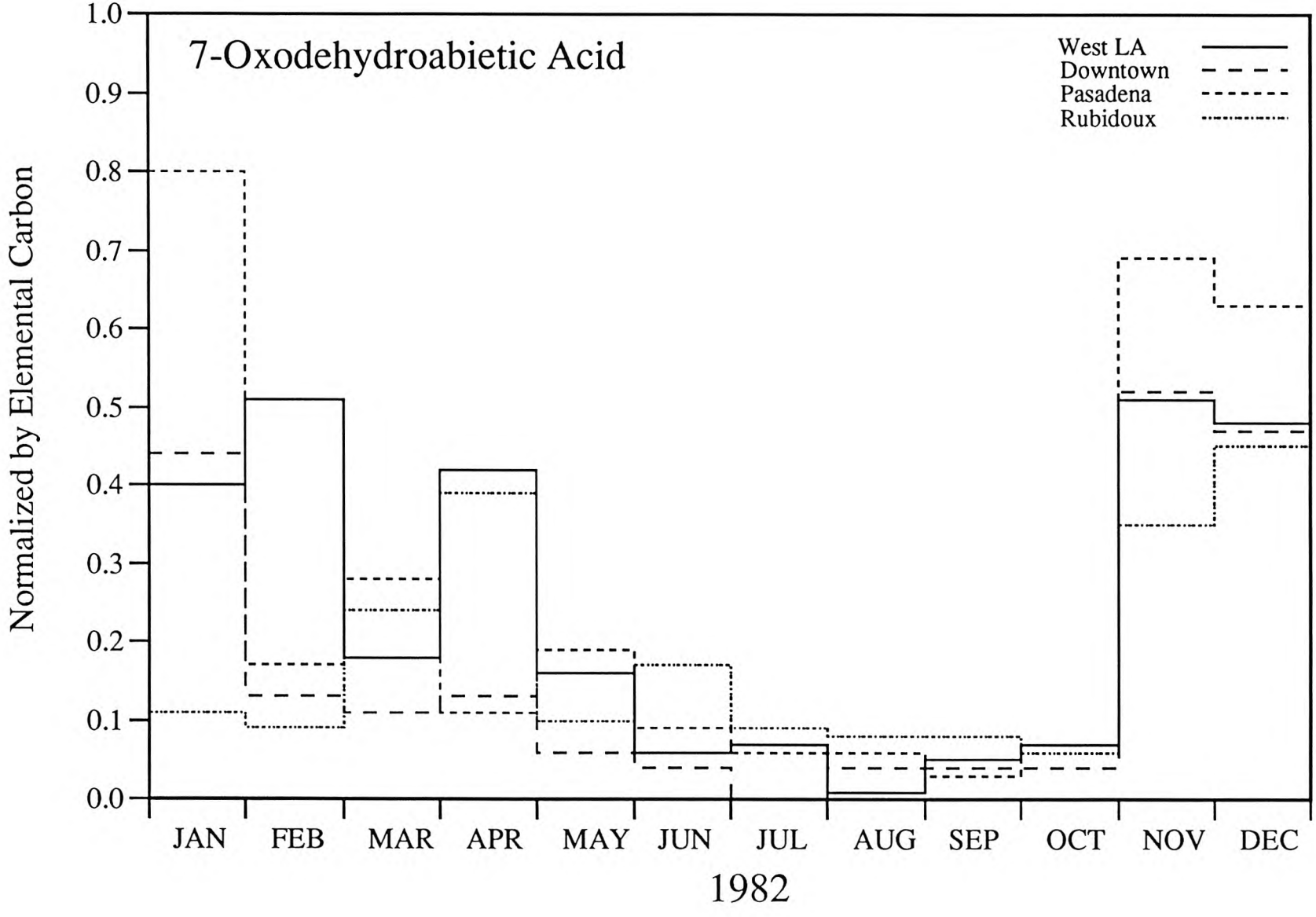
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


7-Oxodehydroabietic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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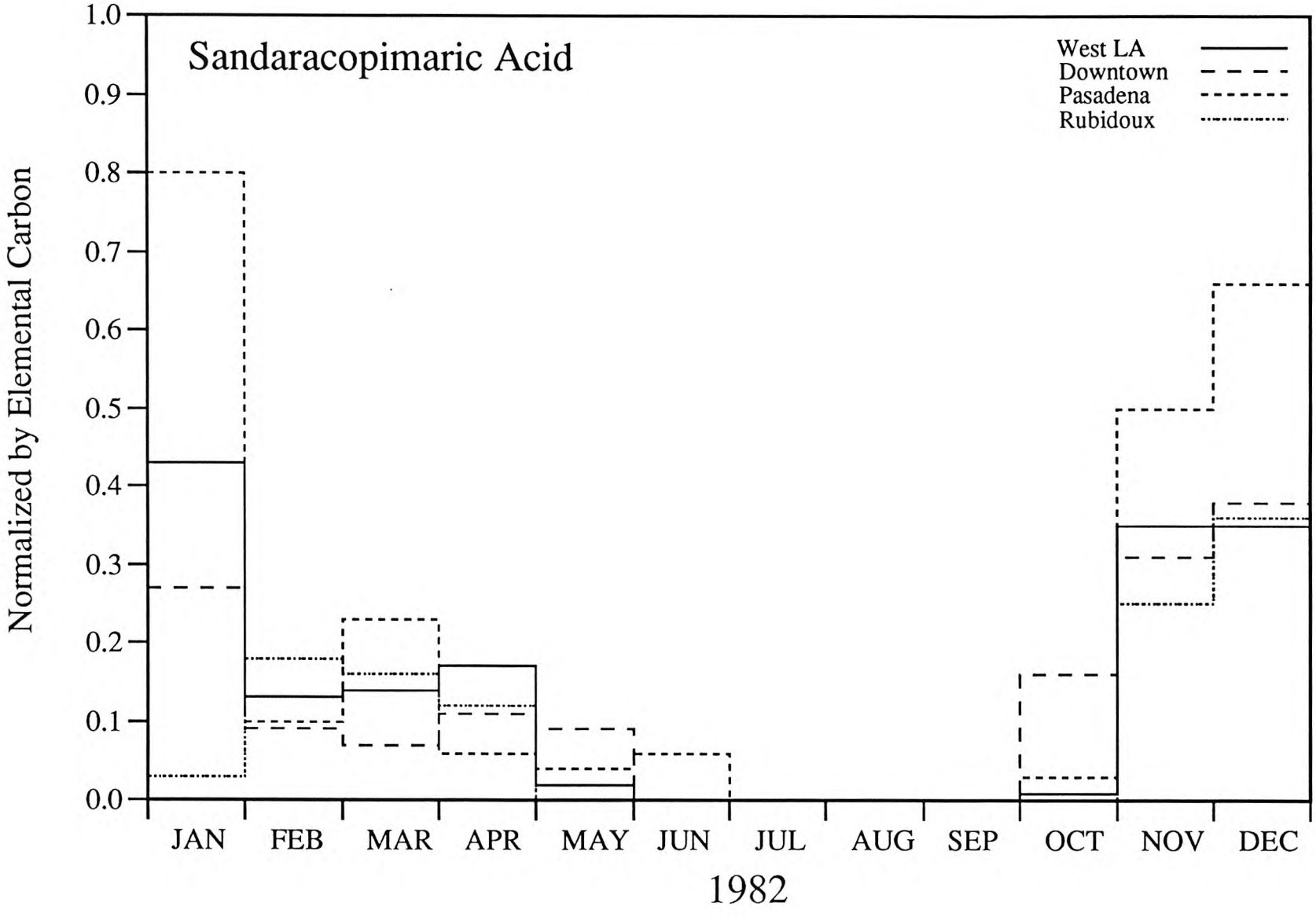
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Sandaracopimaric Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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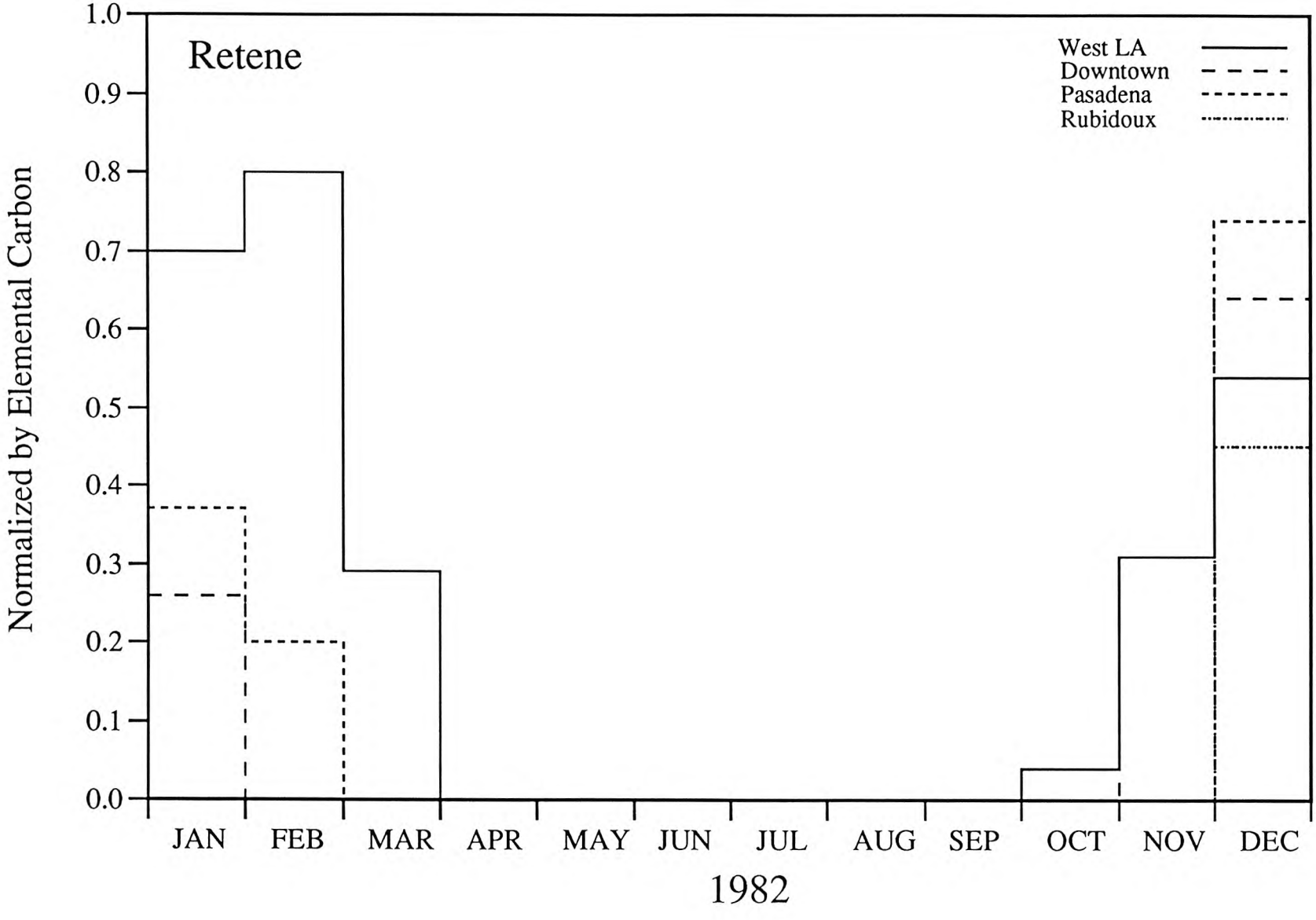
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Retene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
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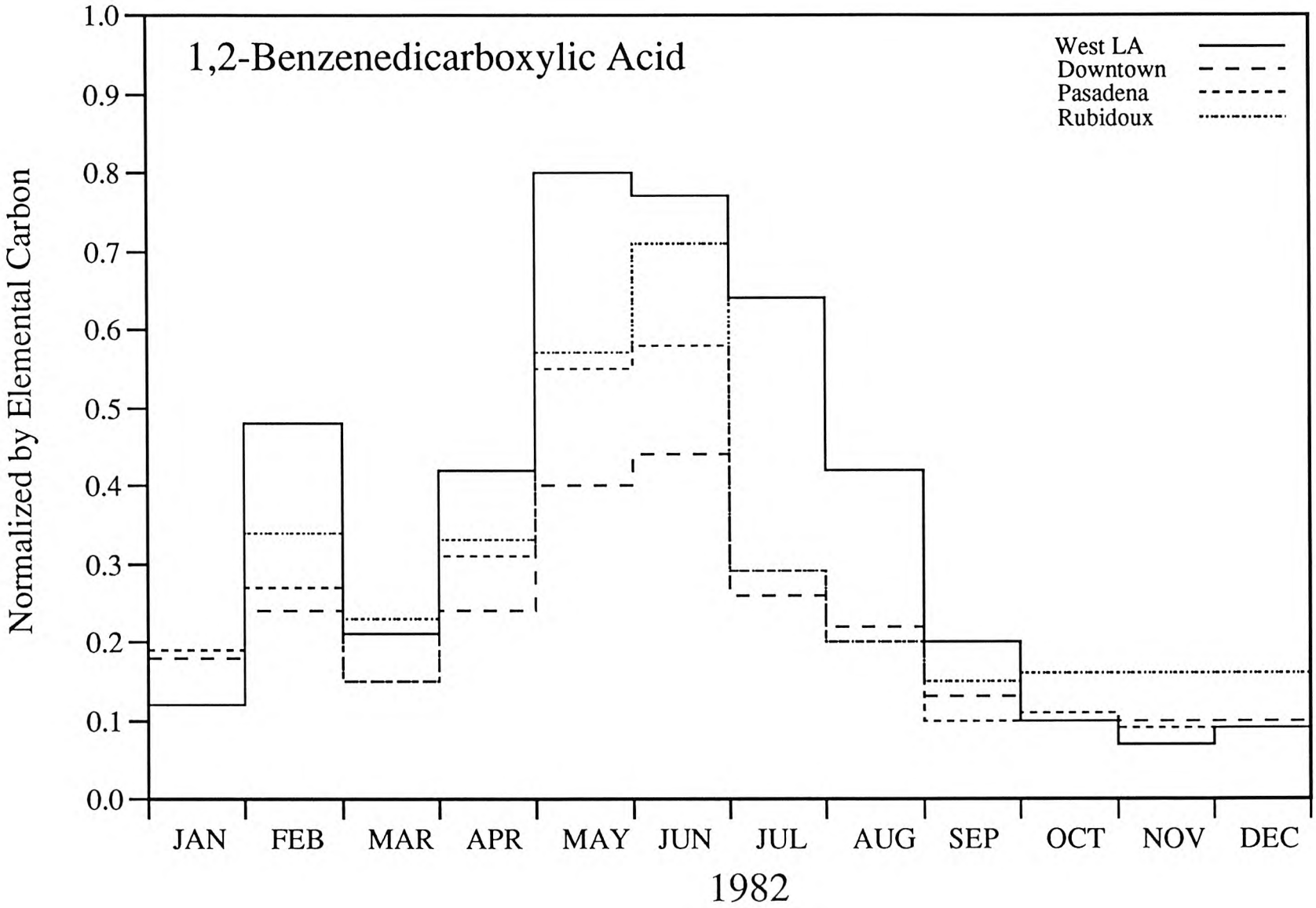
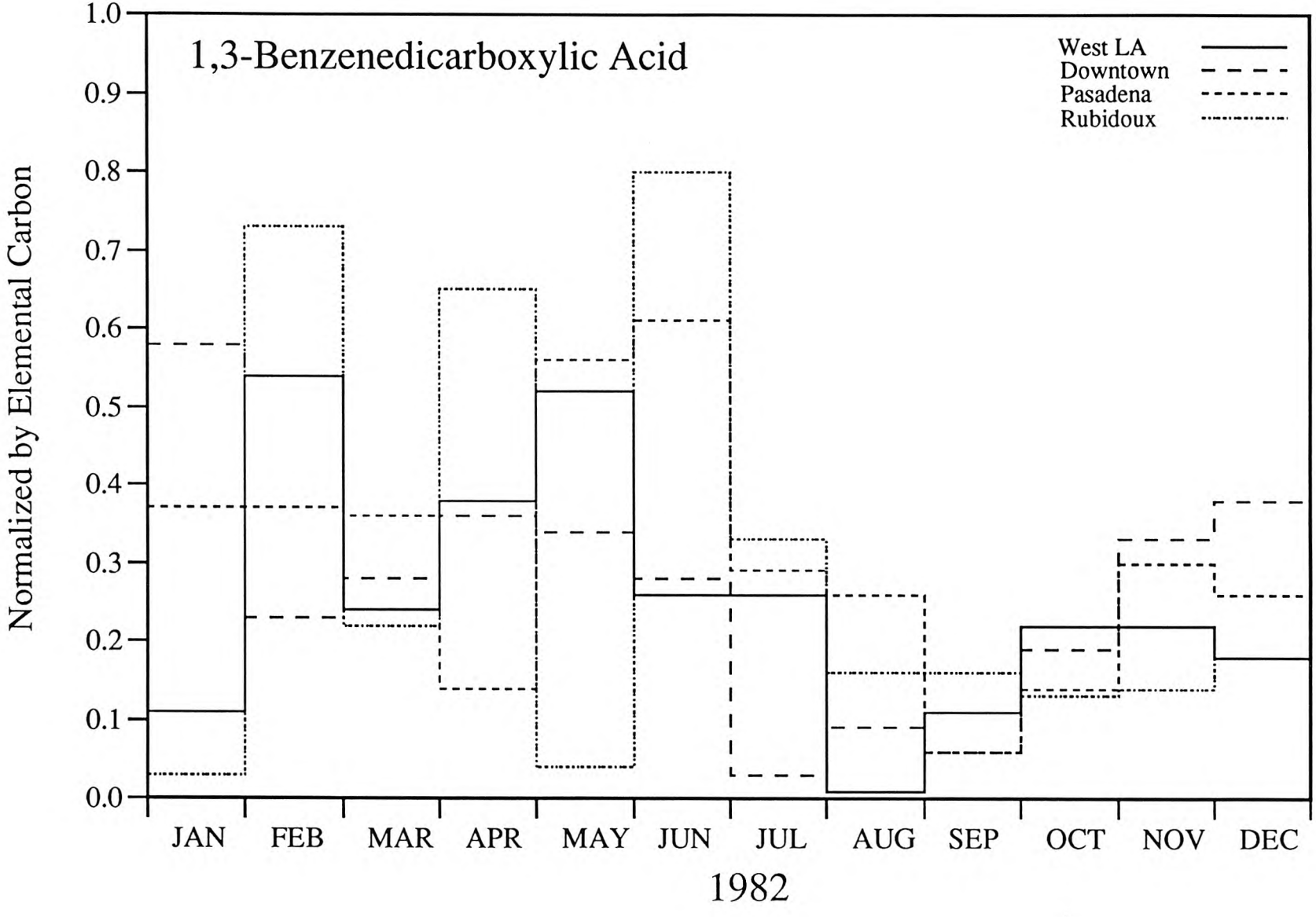
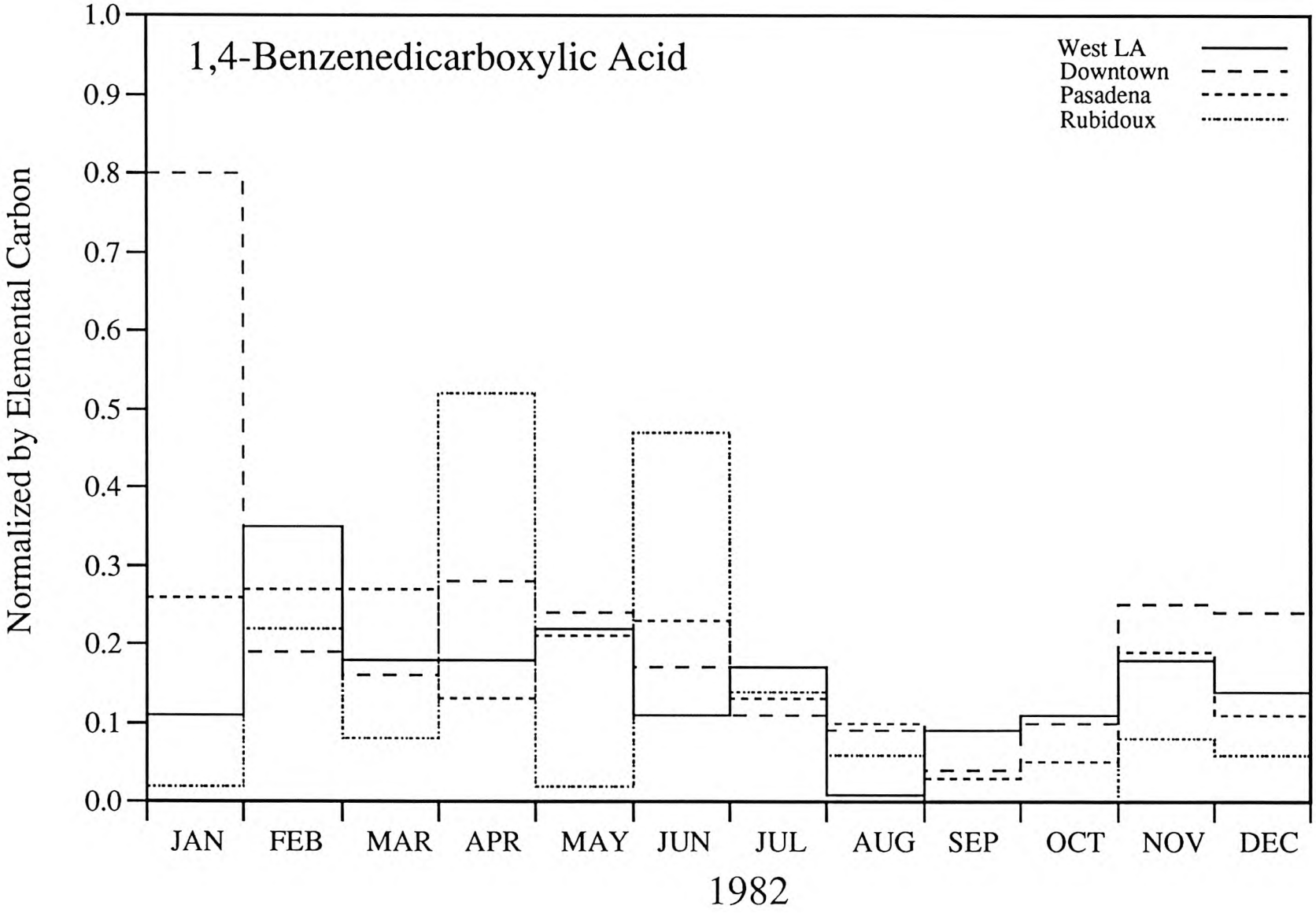
JUL
AUG
SEP
OCT
NOV
DEC
1982

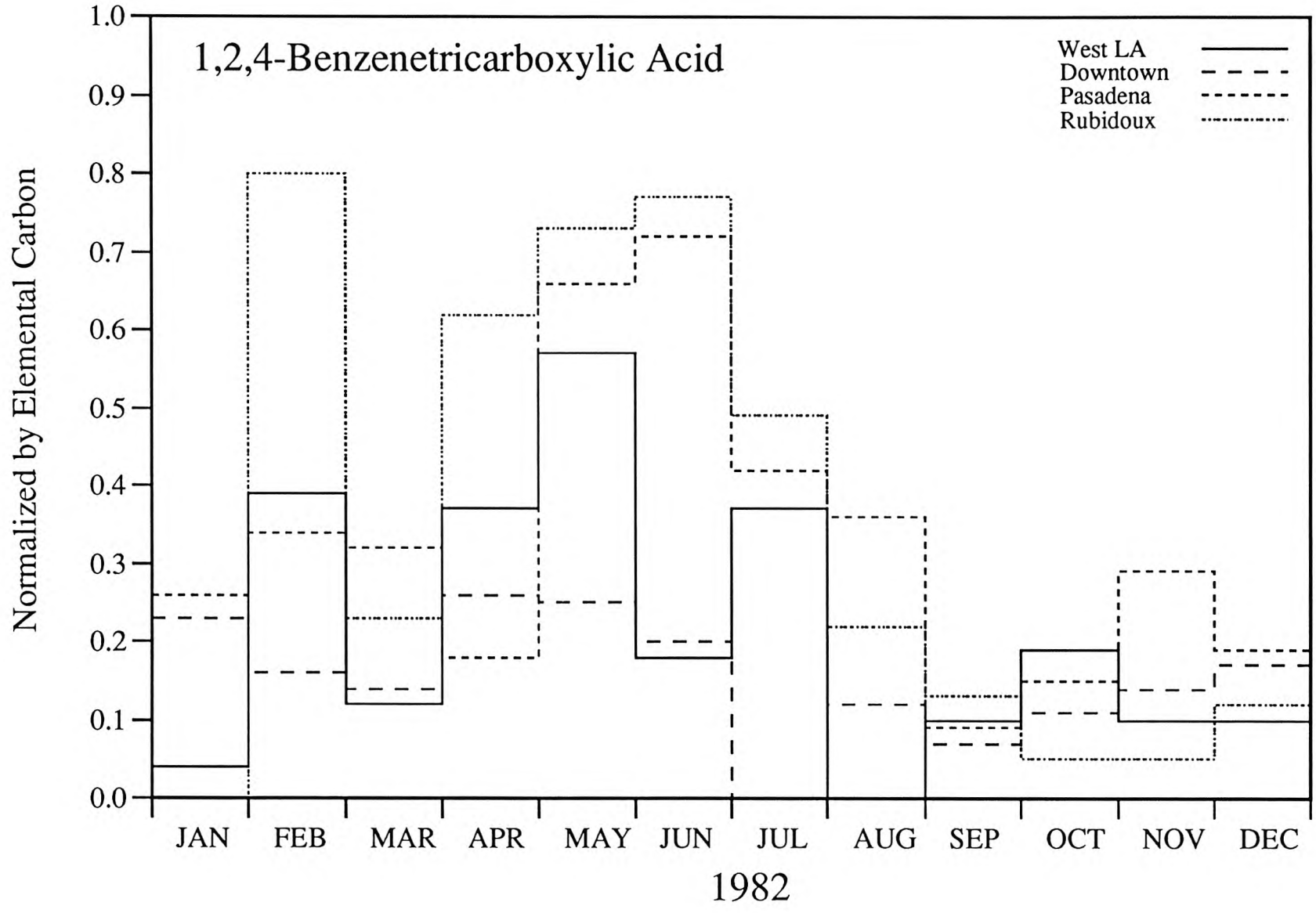
Appendix B7

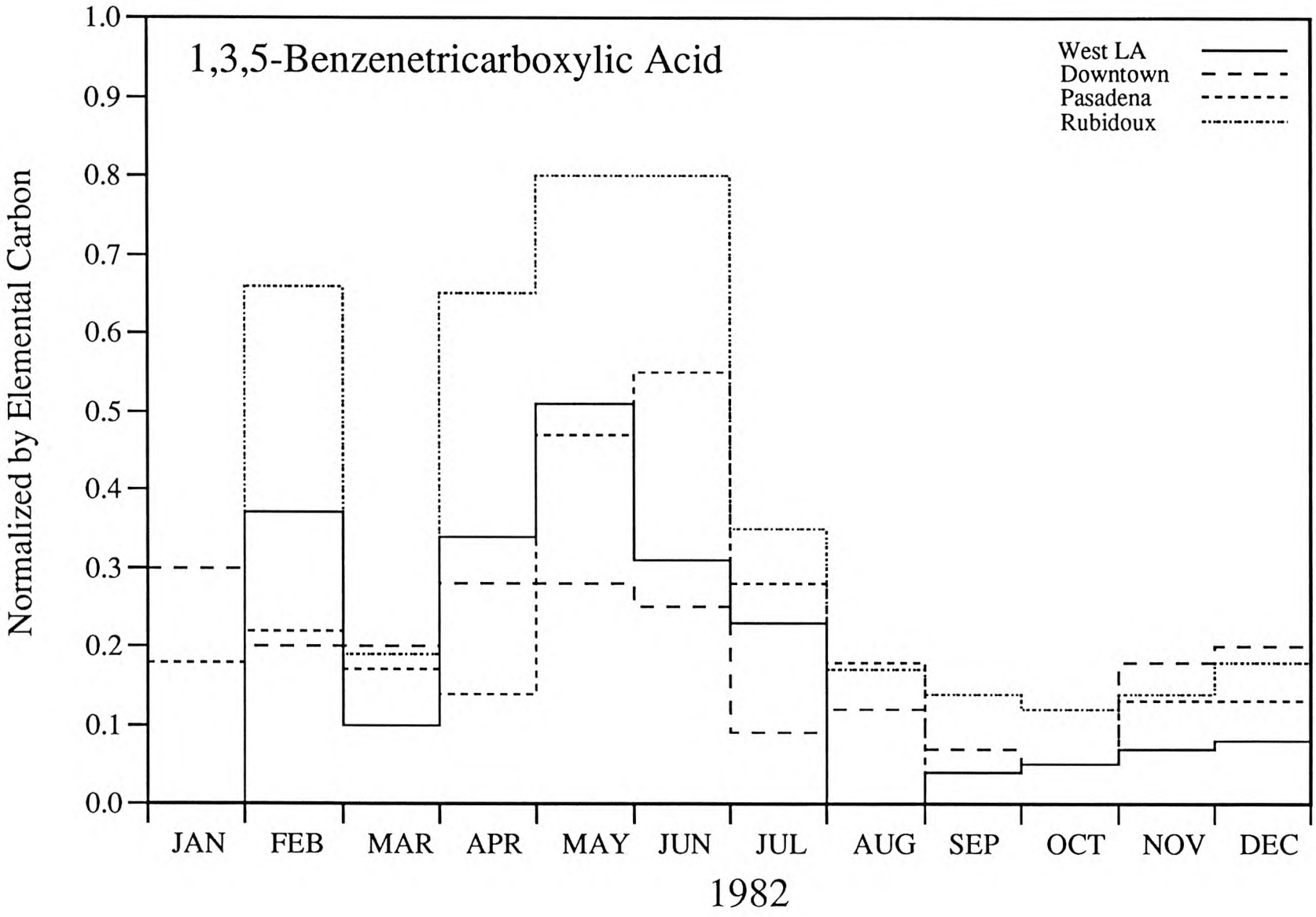
Normalized Concentration Profiles for Aromatic Polycarboxylic Acids

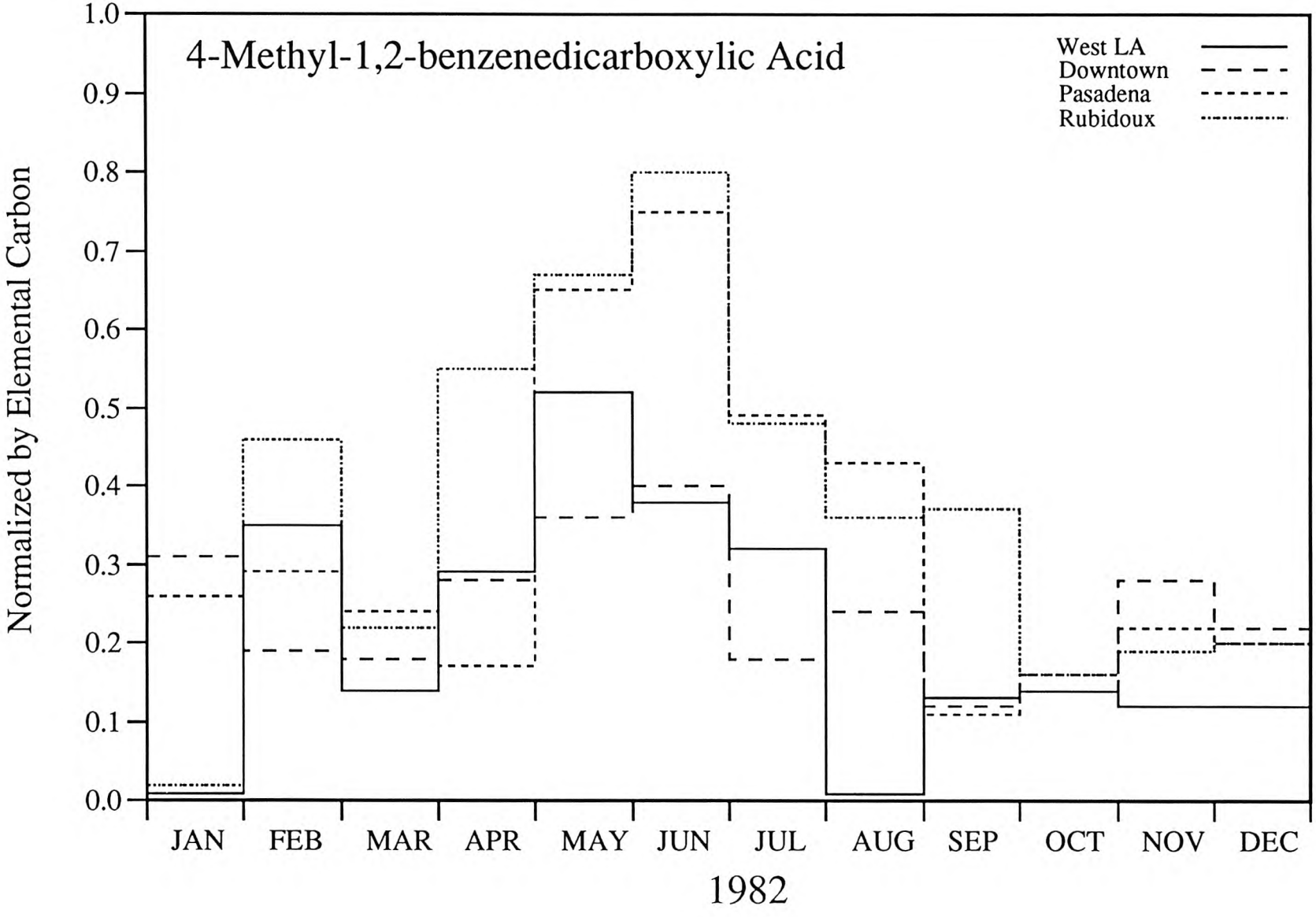

1,2-Benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

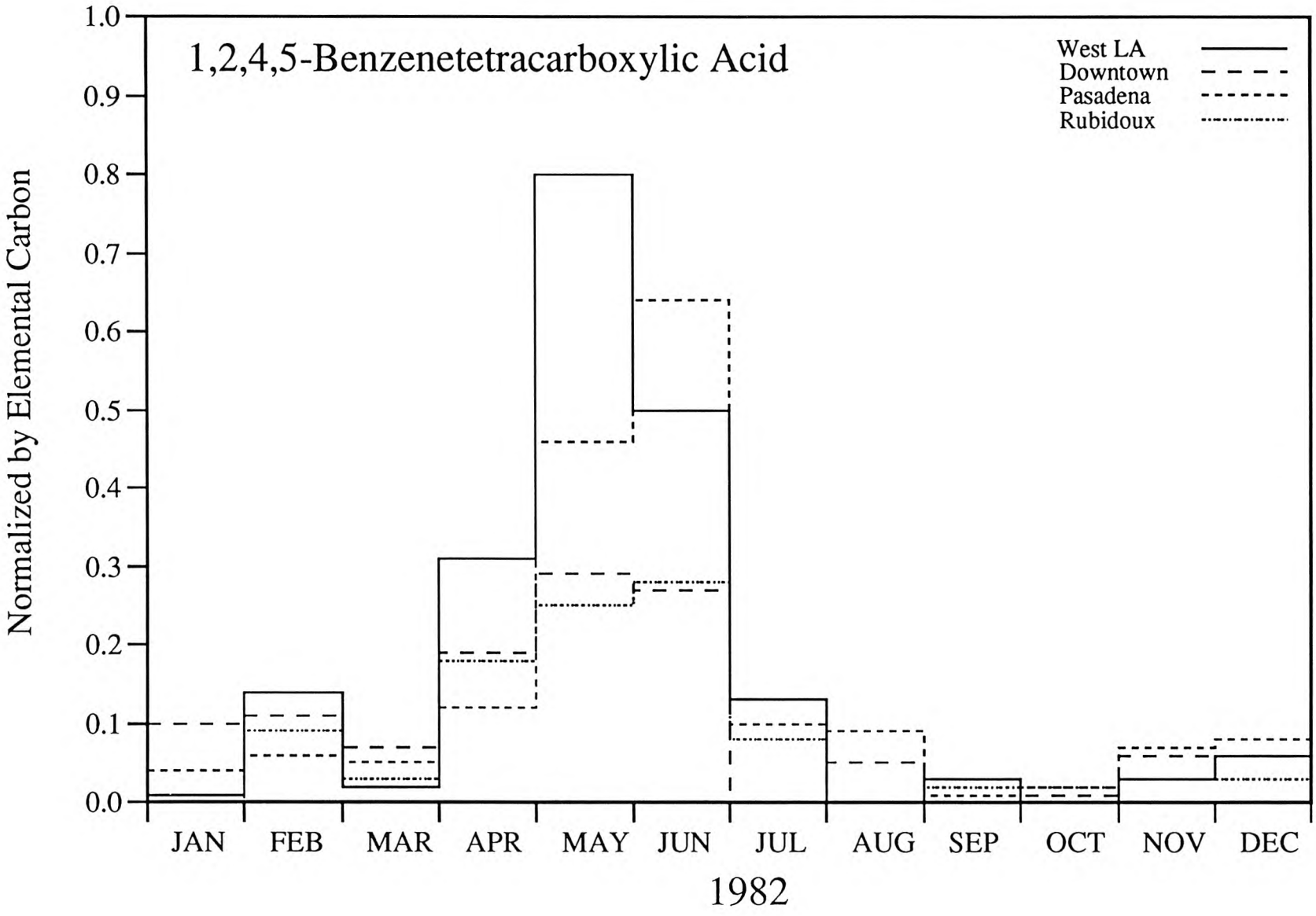

1,3-Benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


1,4-Benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


1,2,4-Benzenetricarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

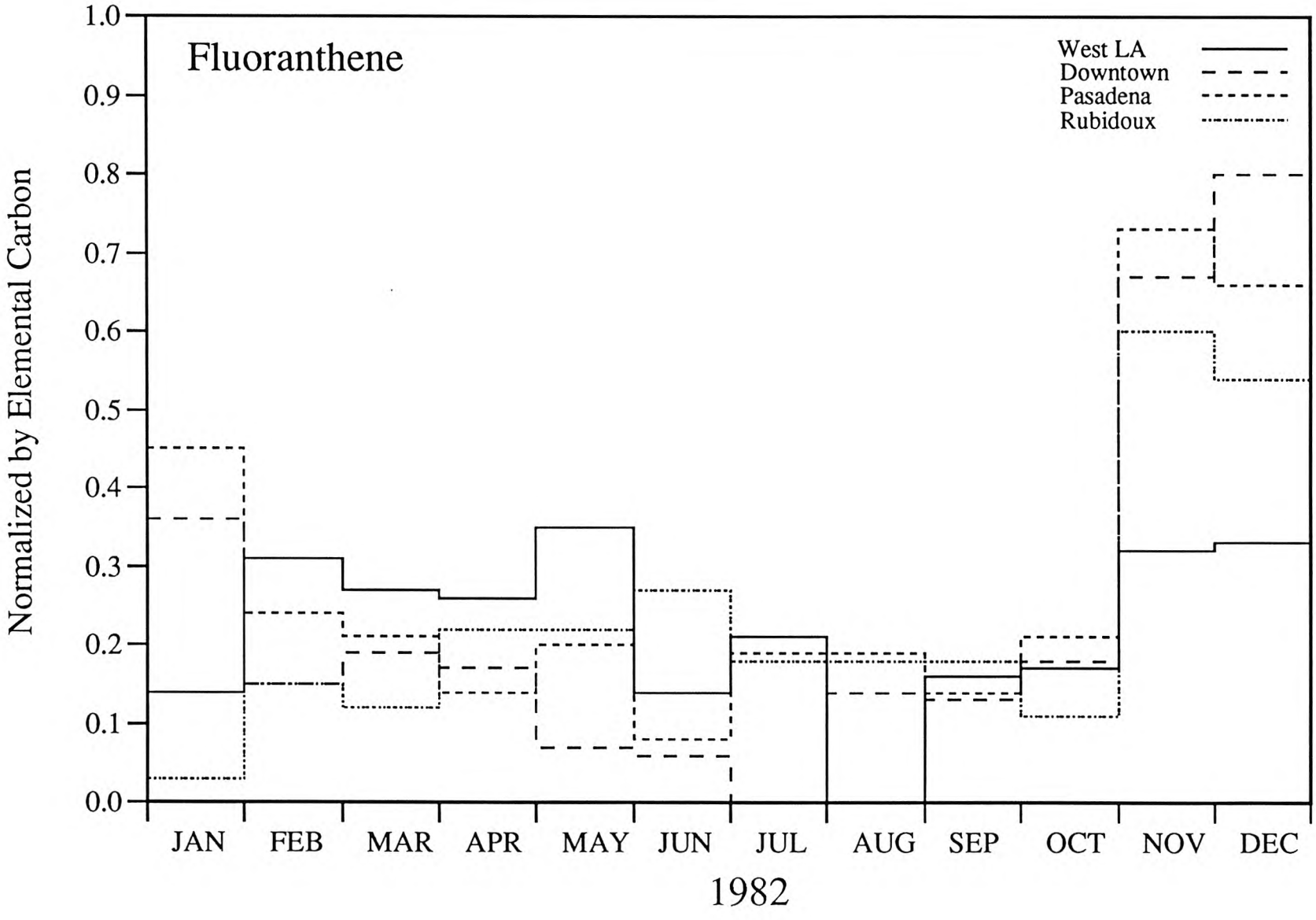

1,3,5-Benzenetricarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

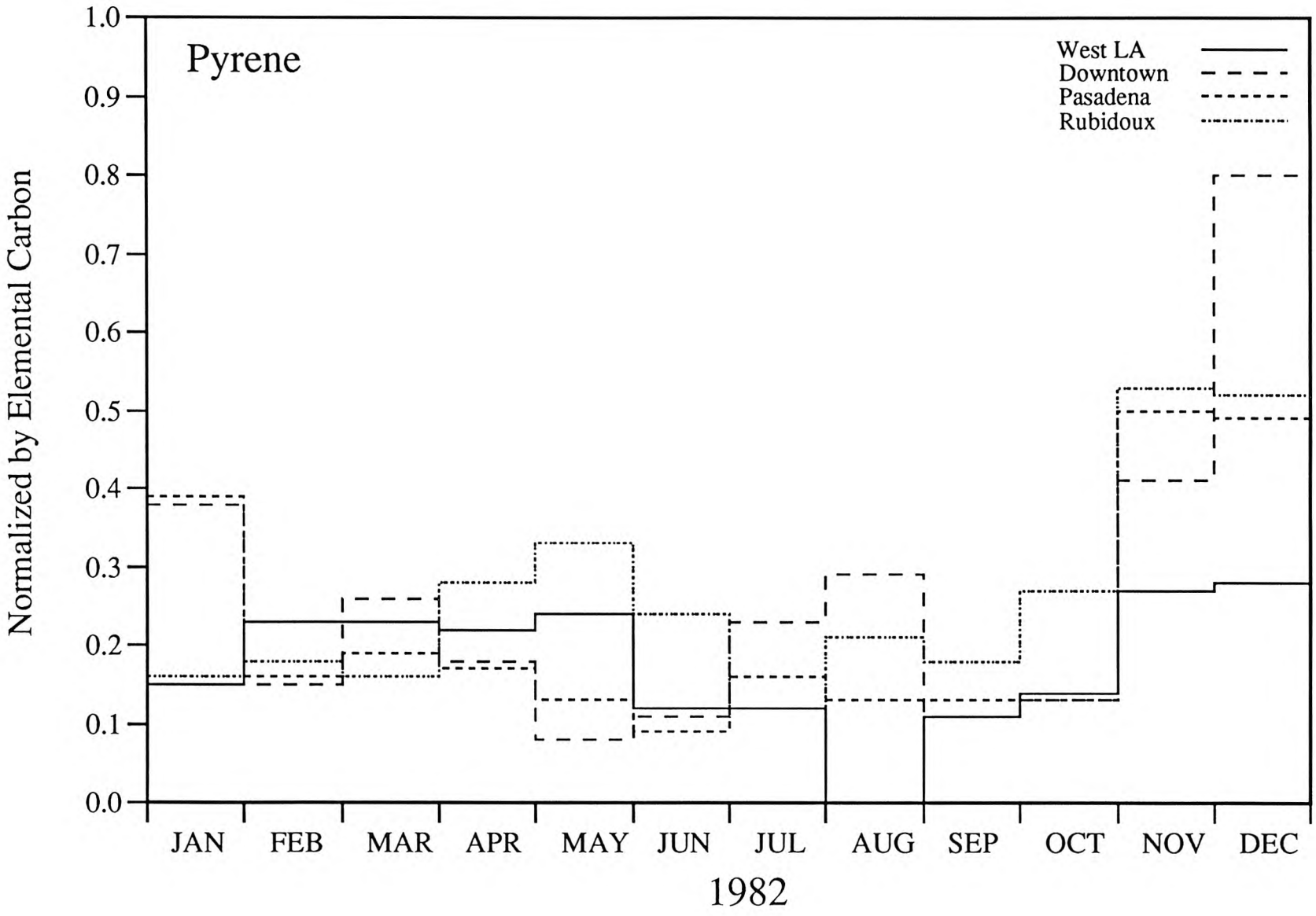

4-Methyl-1,2-benzenedicarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

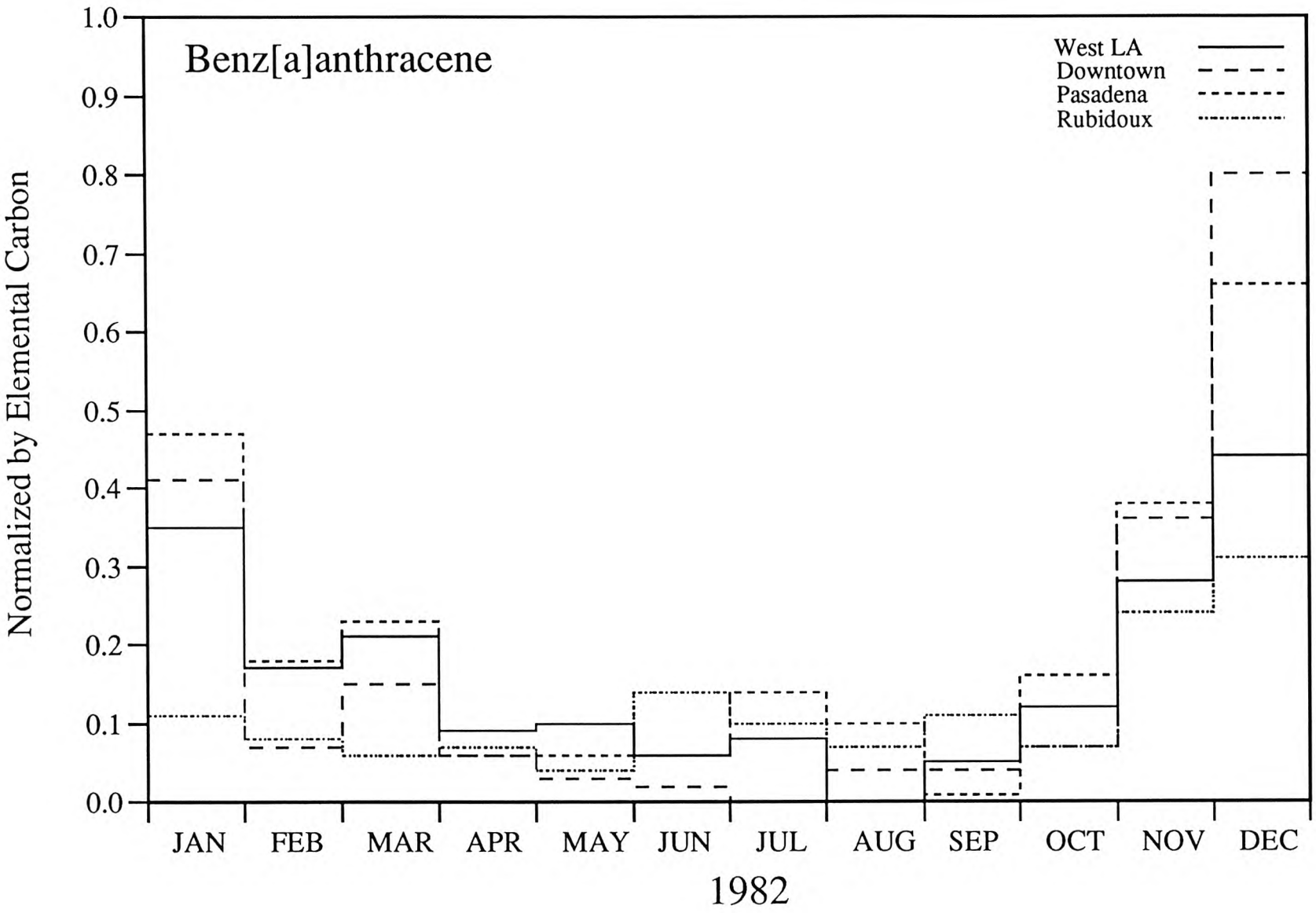

1,2,4,5-Benzenetetracarboxylic Acid
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

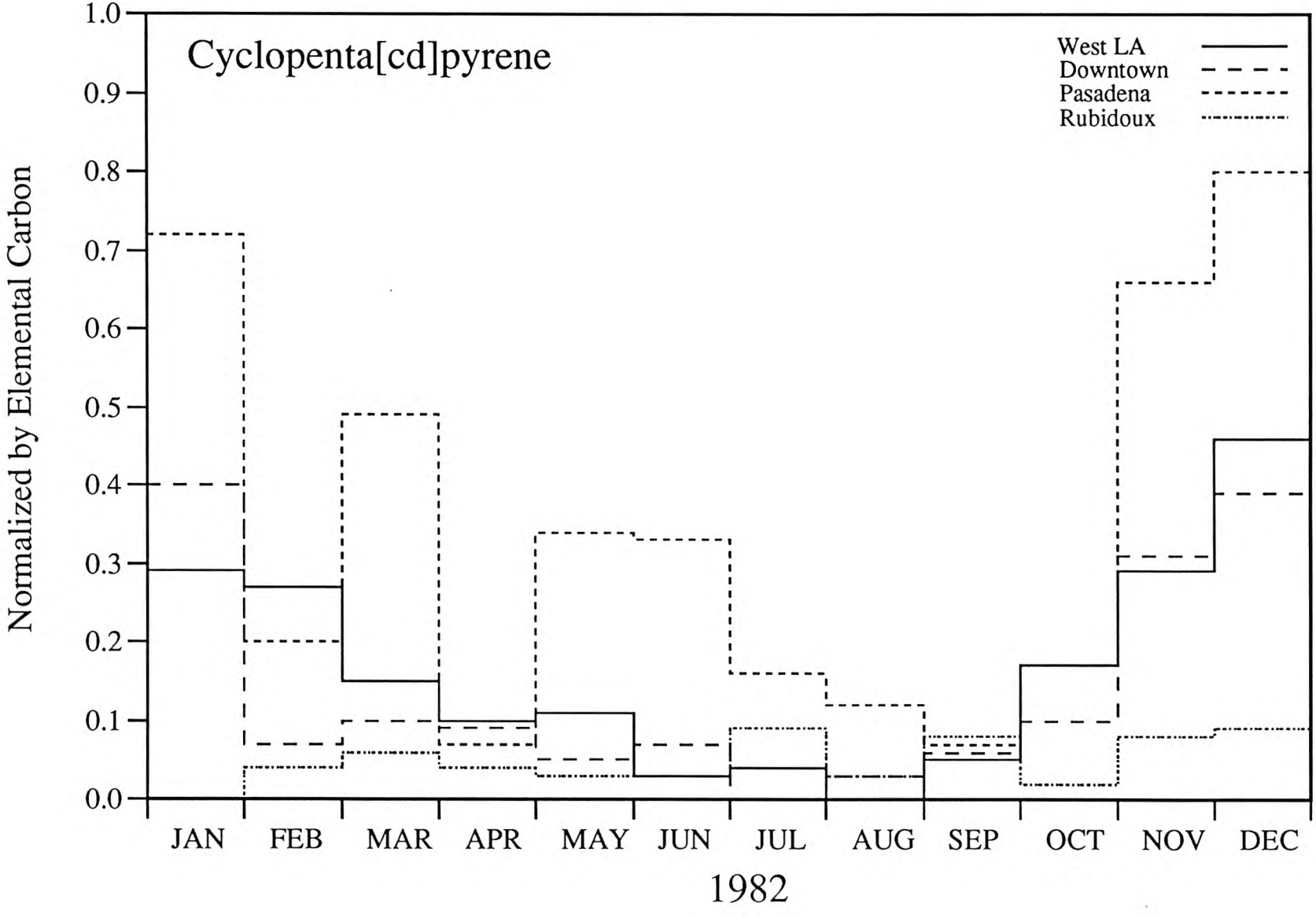
Appendix B8

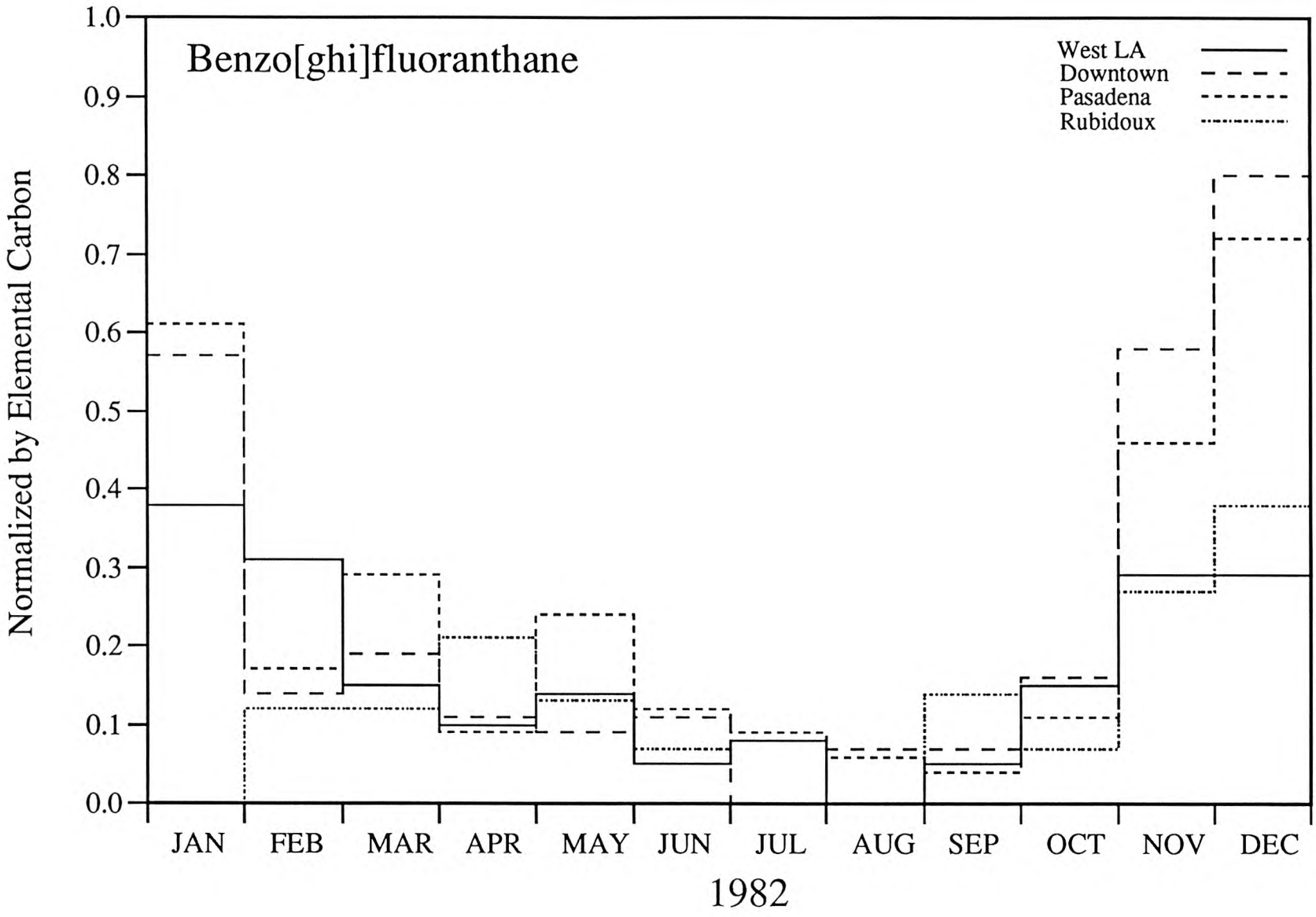
Normalized Concentration Profiles for Polycyclic Aromatic Hydrocarbons PAH's

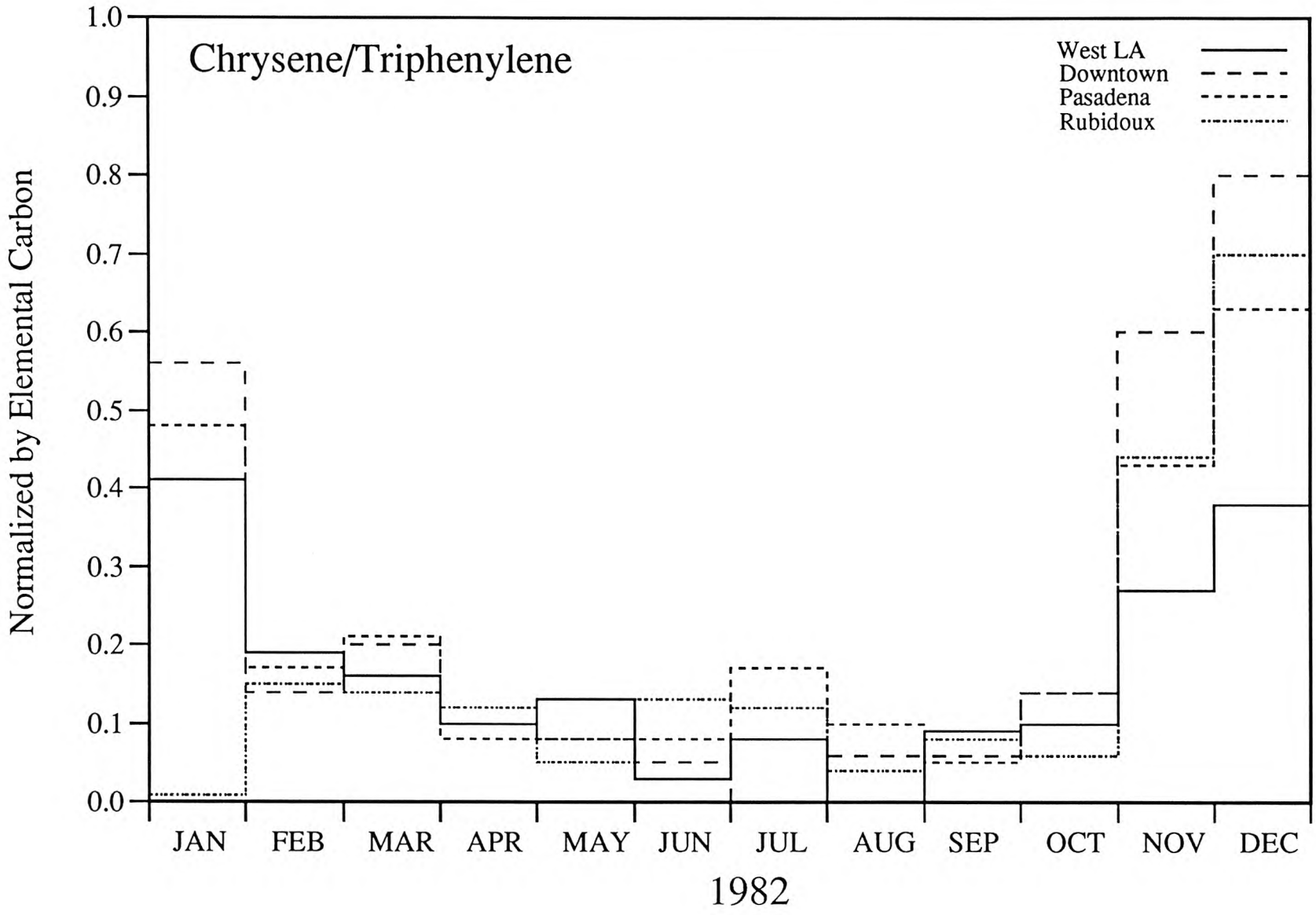

Fluoranthene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

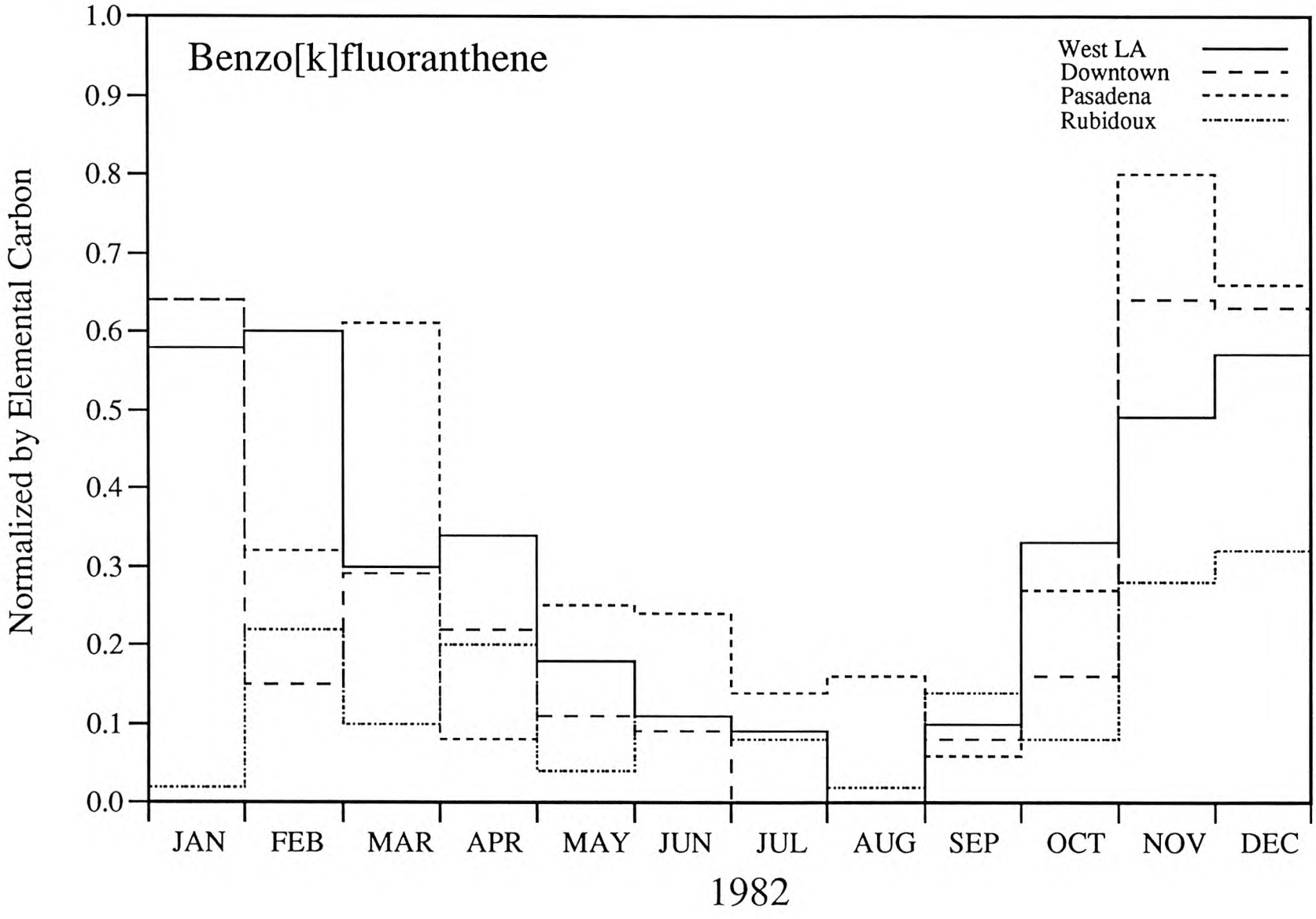

Pyrene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

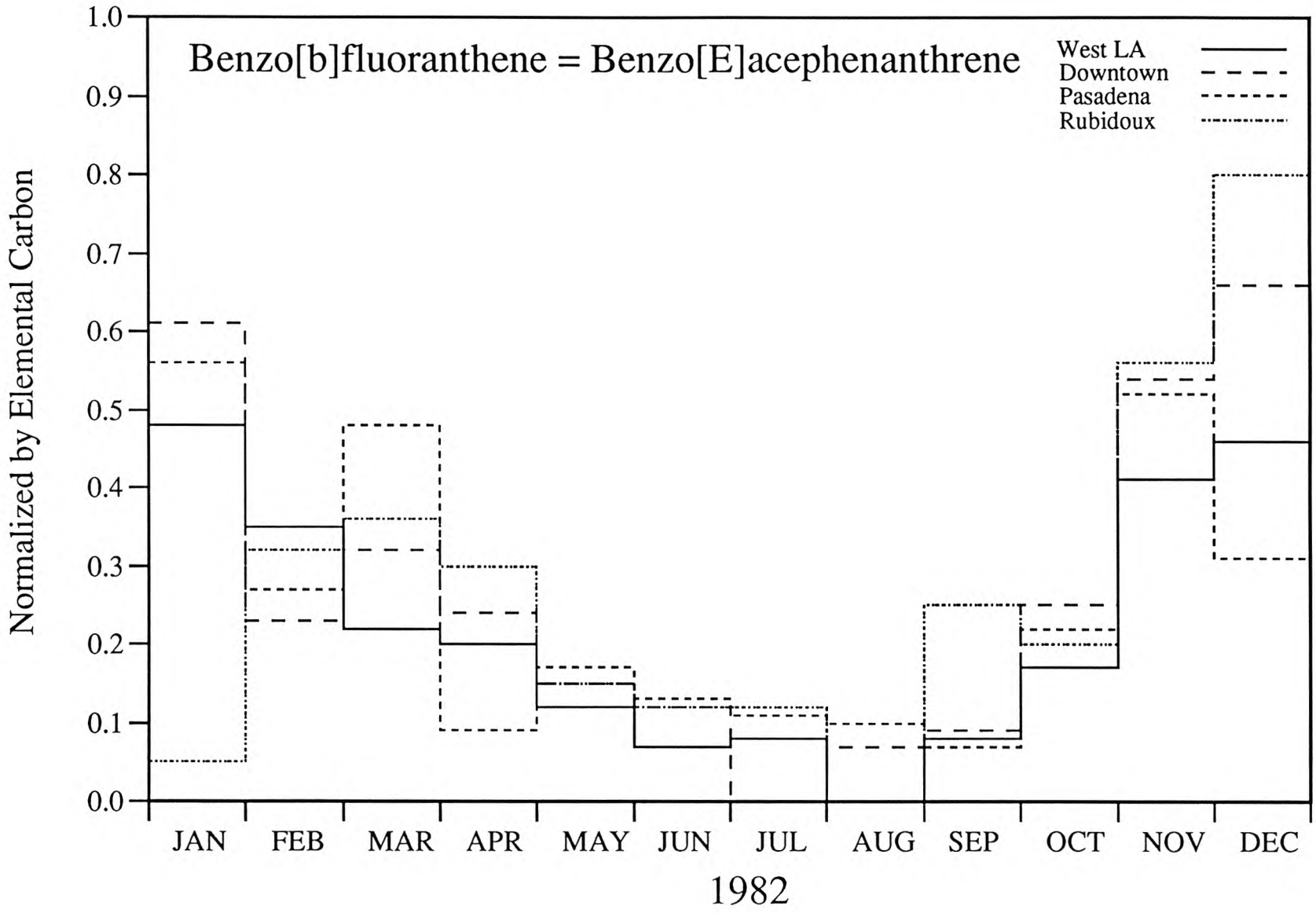

Benz[a]anthracene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

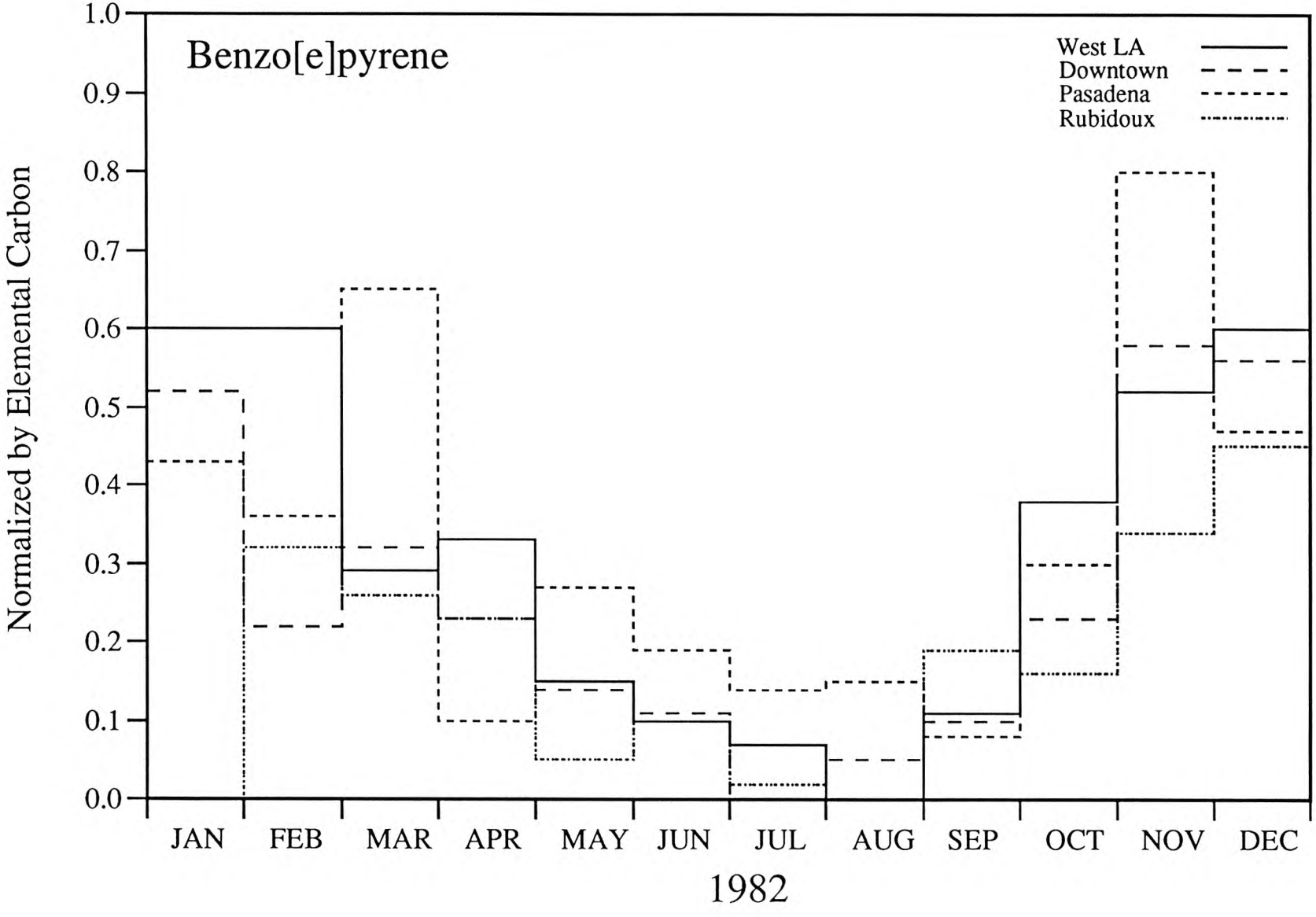

Cyclopenta[cd]pyrene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

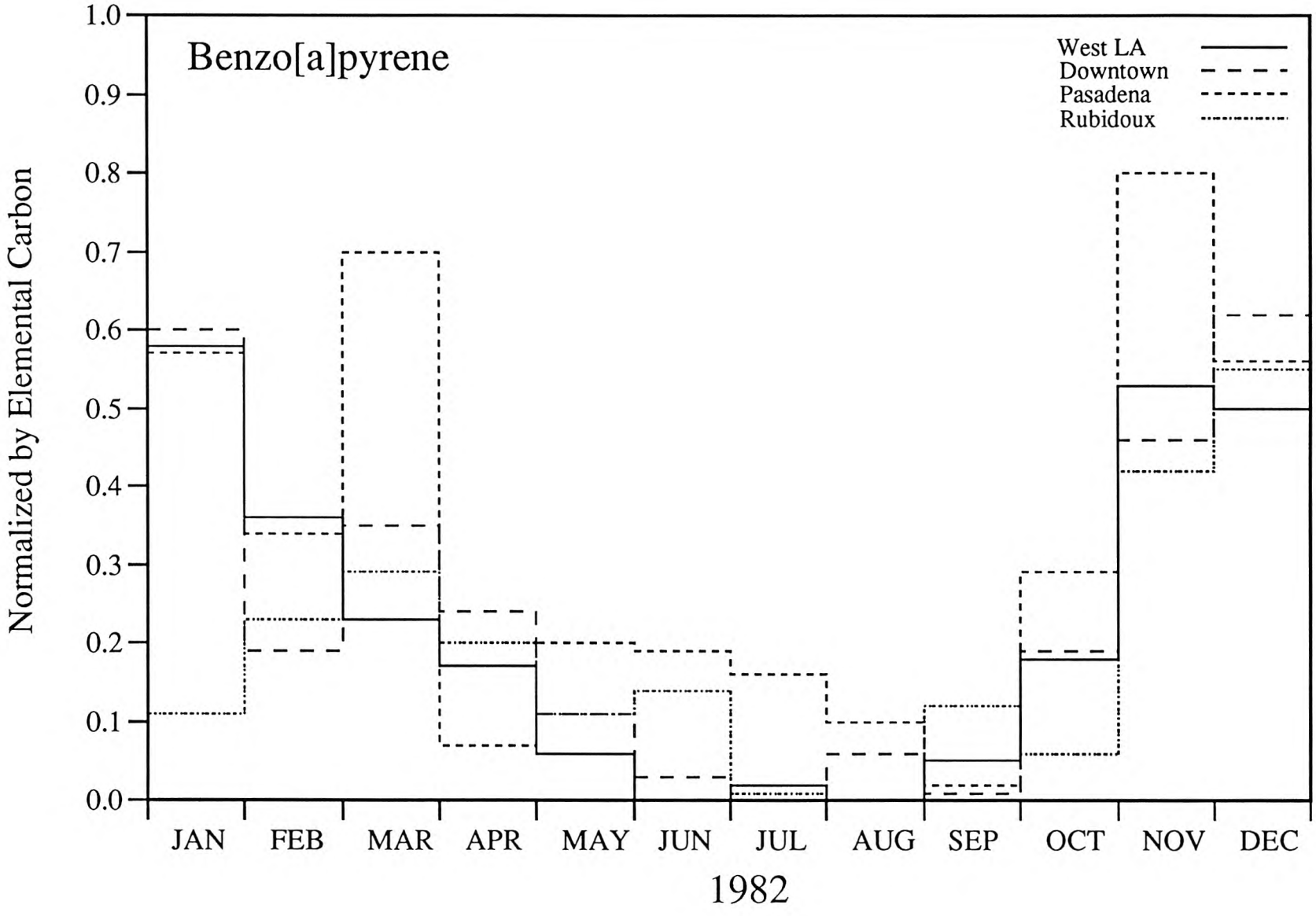

Benzo[ghi]fluoranthane
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

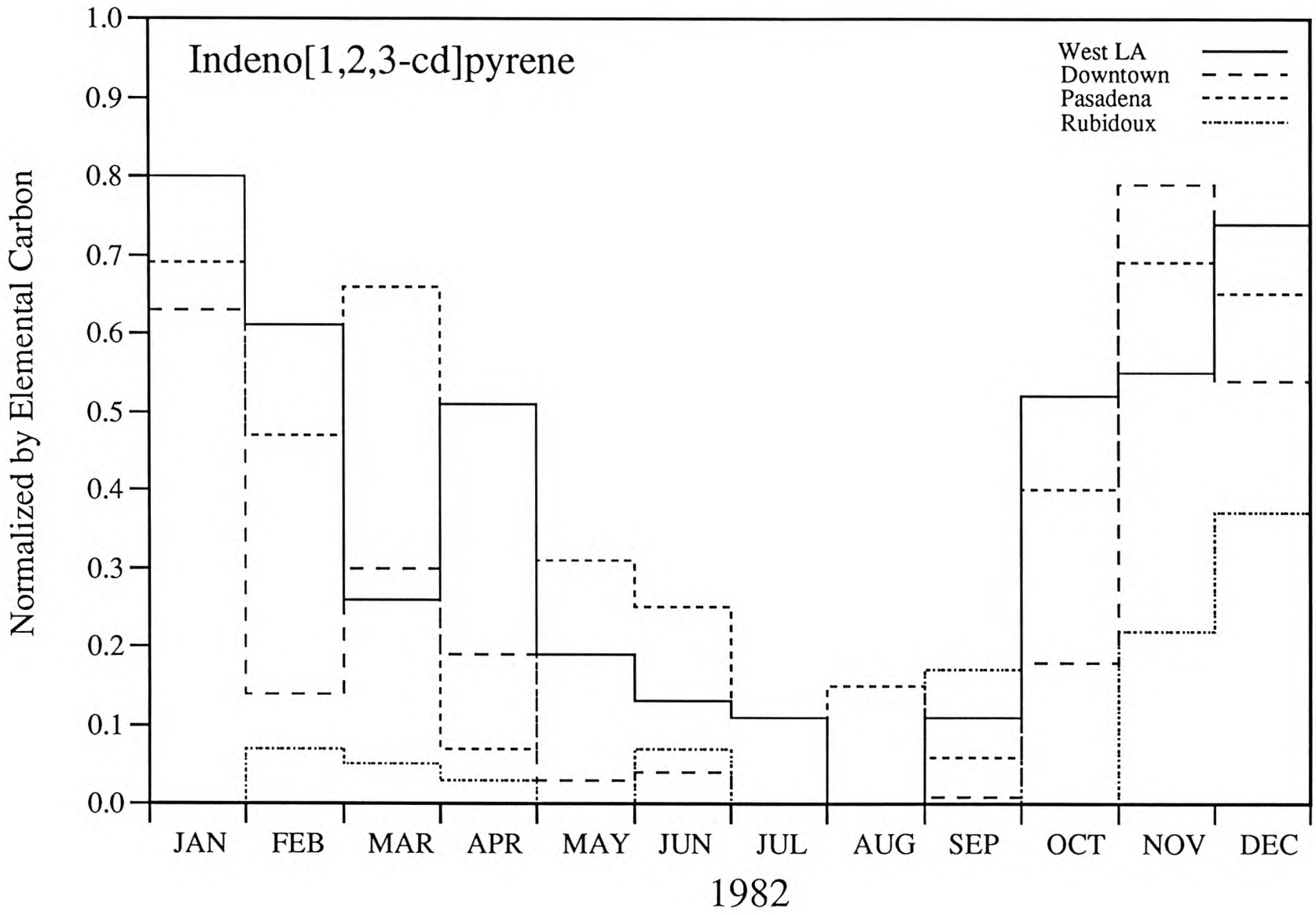

Chrysene/Triphenylene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

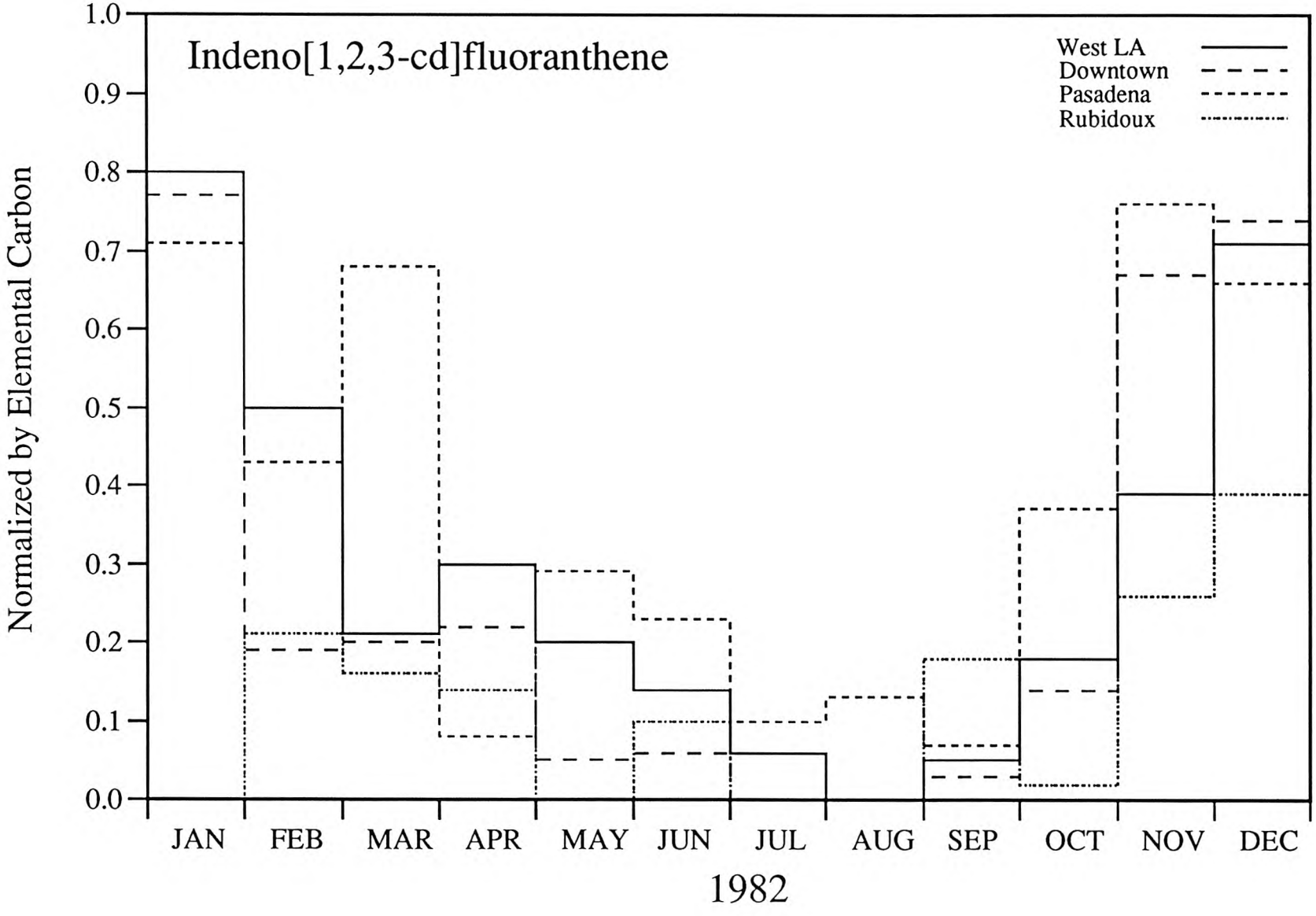

Benzo[k]fluoranthene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

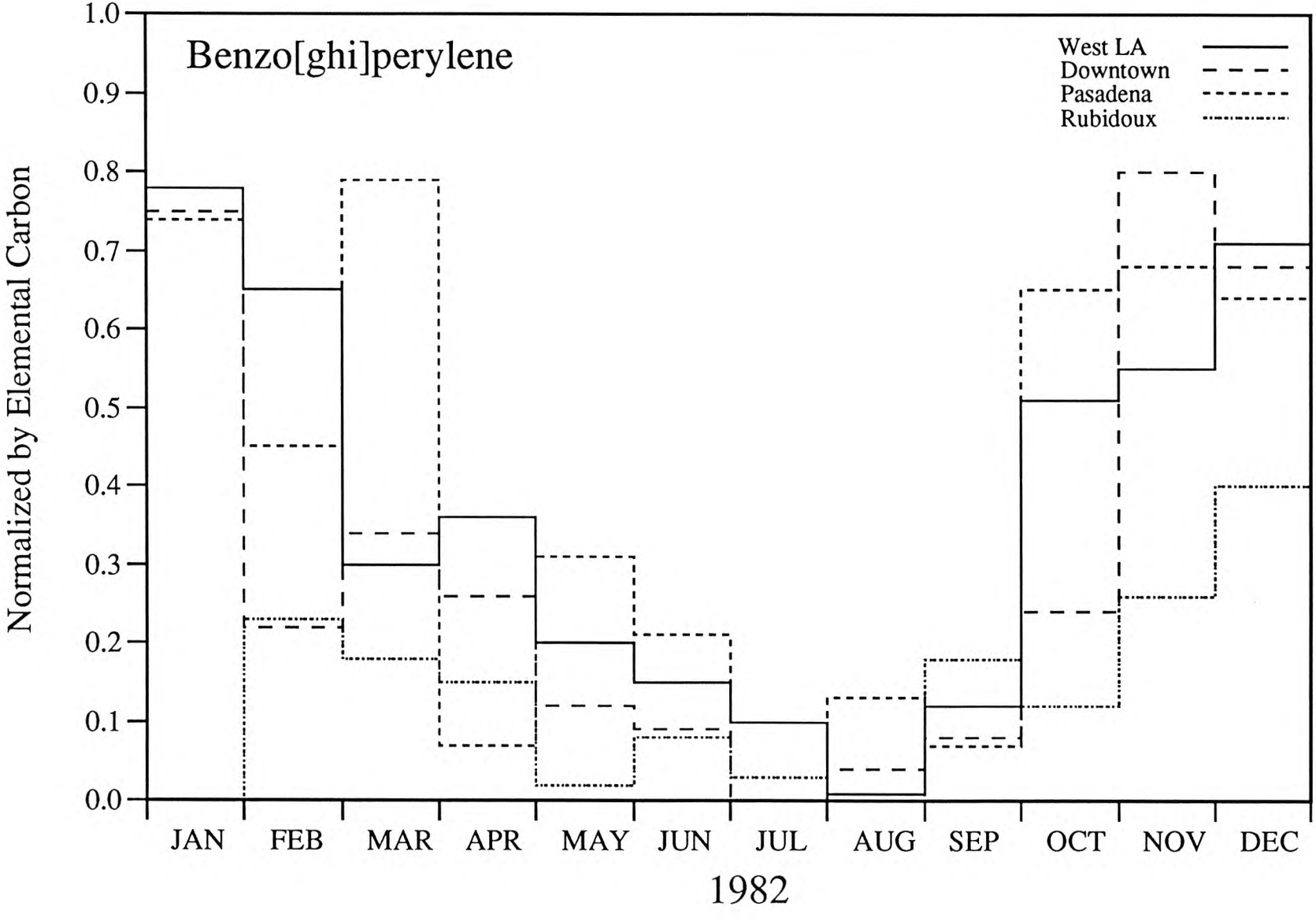

Benzo[b]fluoranthene = Benzo[E]acephenanthrene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

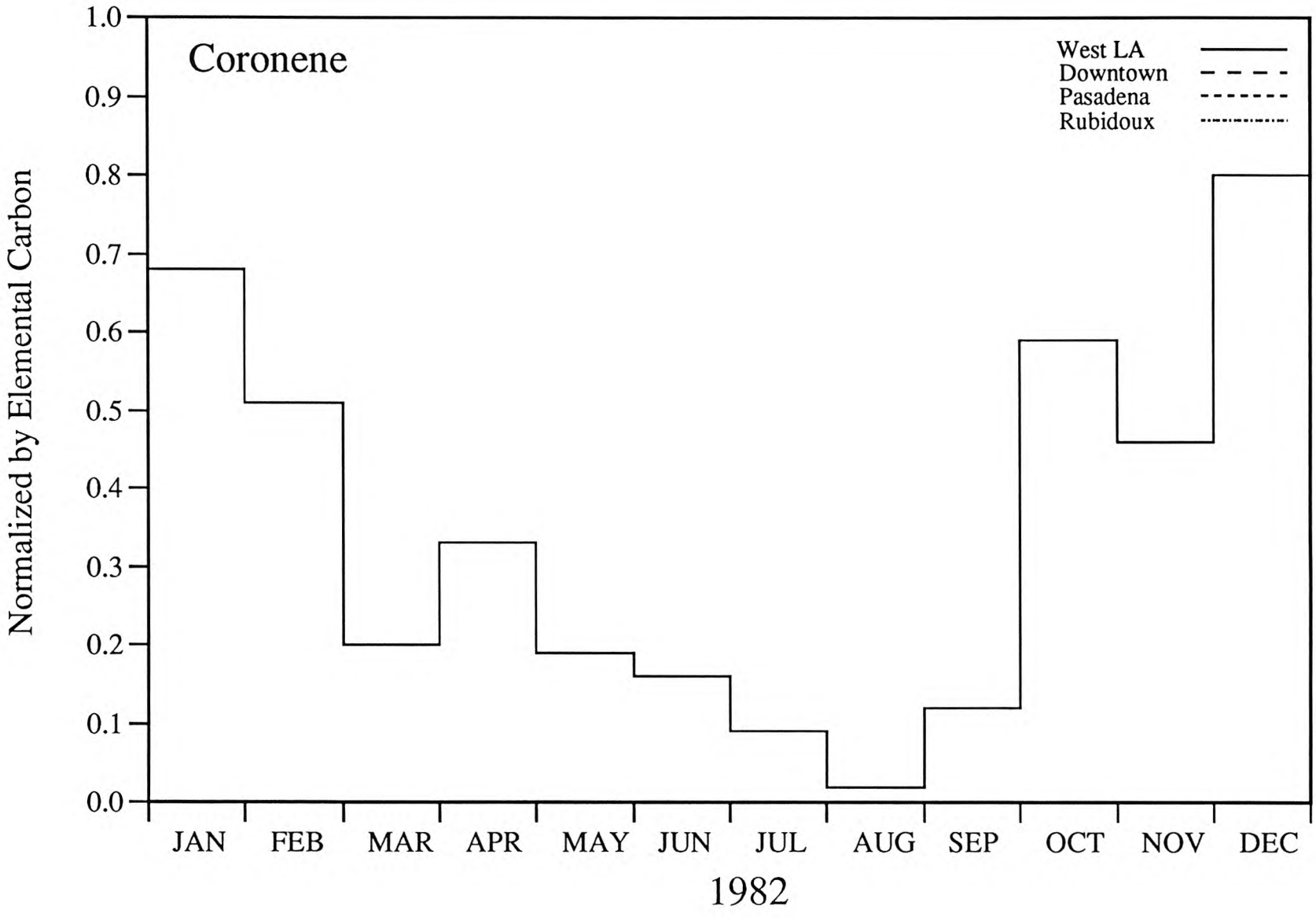

Benzo[e]pyrene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Benzo[a]pyrene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Indeno[1,2,3-cd]pyrene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

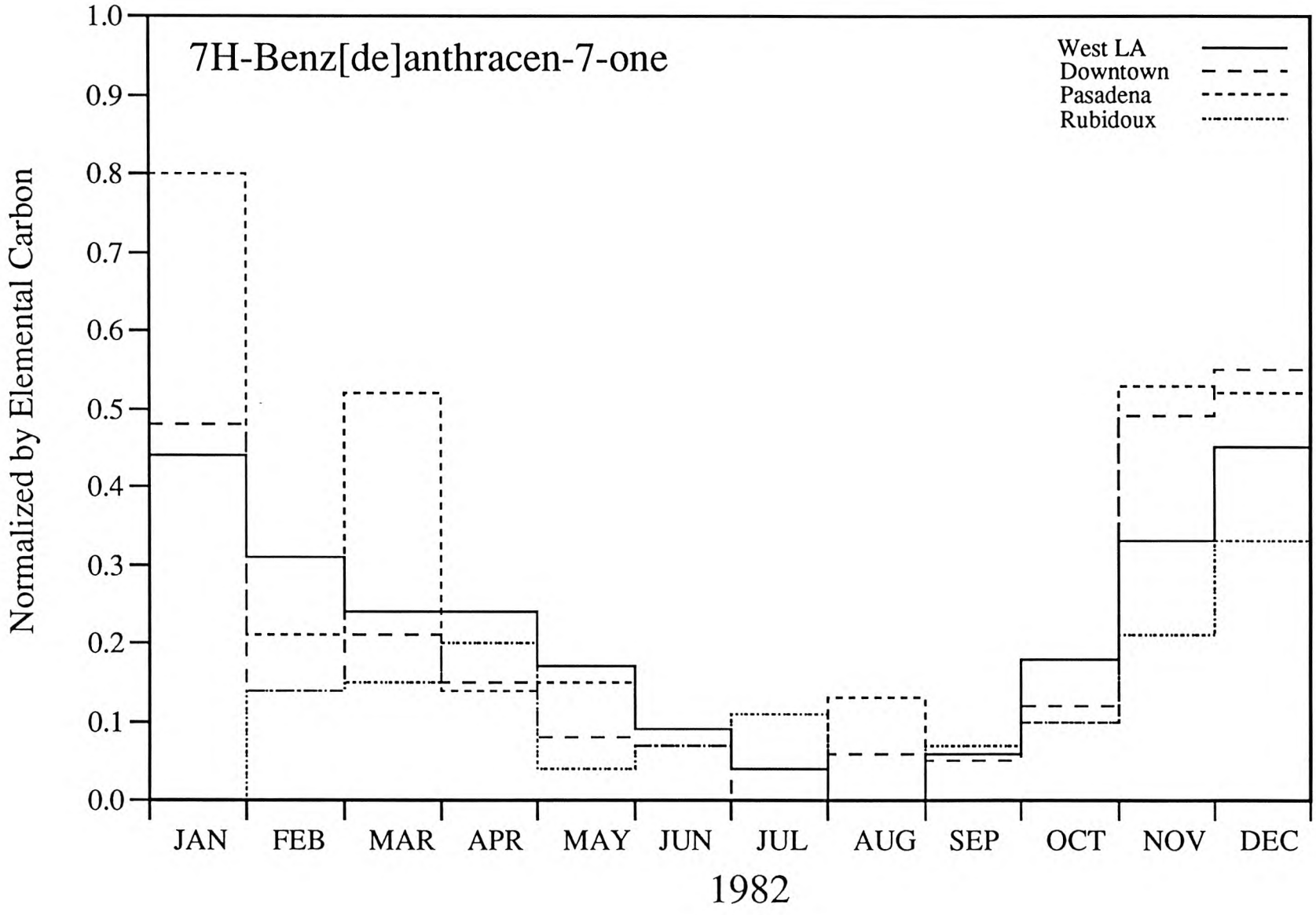

Indeno[1,2,3-cd]fluoranthene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

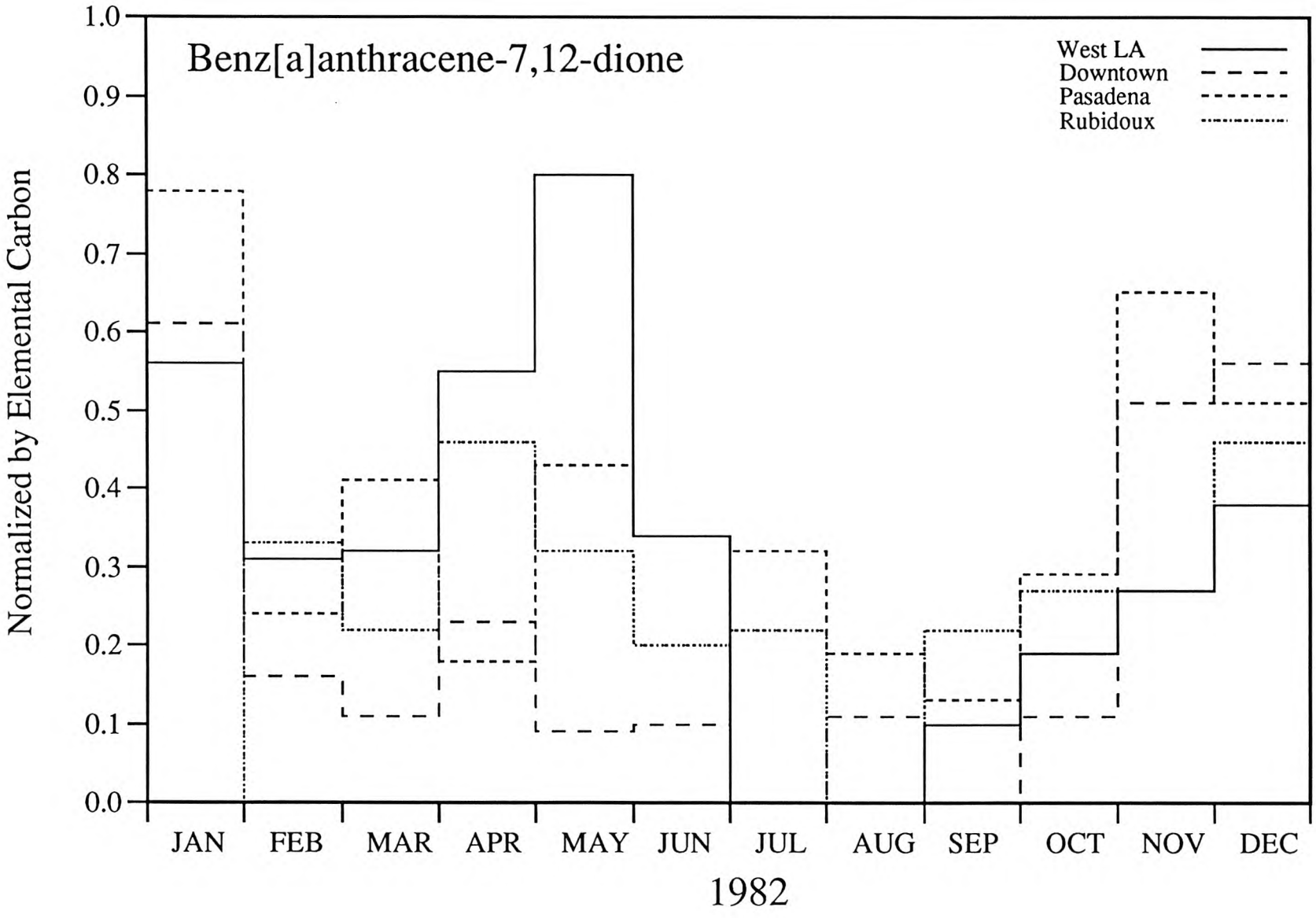

Benzo[ghi]perylene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

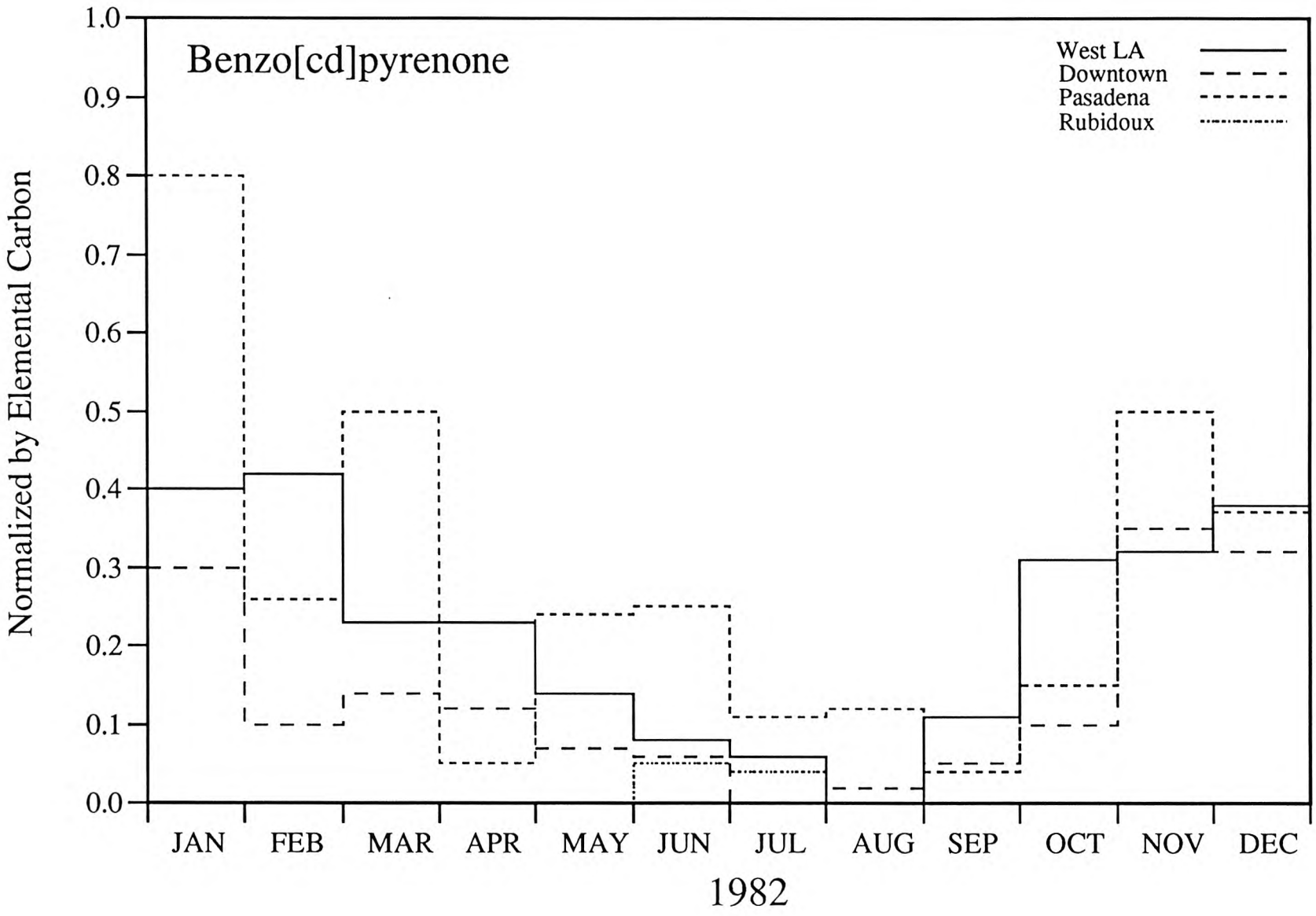

Coronene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

Appendix B9

Normalized Concentration Profiles for Polycyclic Aromatic Ketones and Quinones PAK's + PAQ's

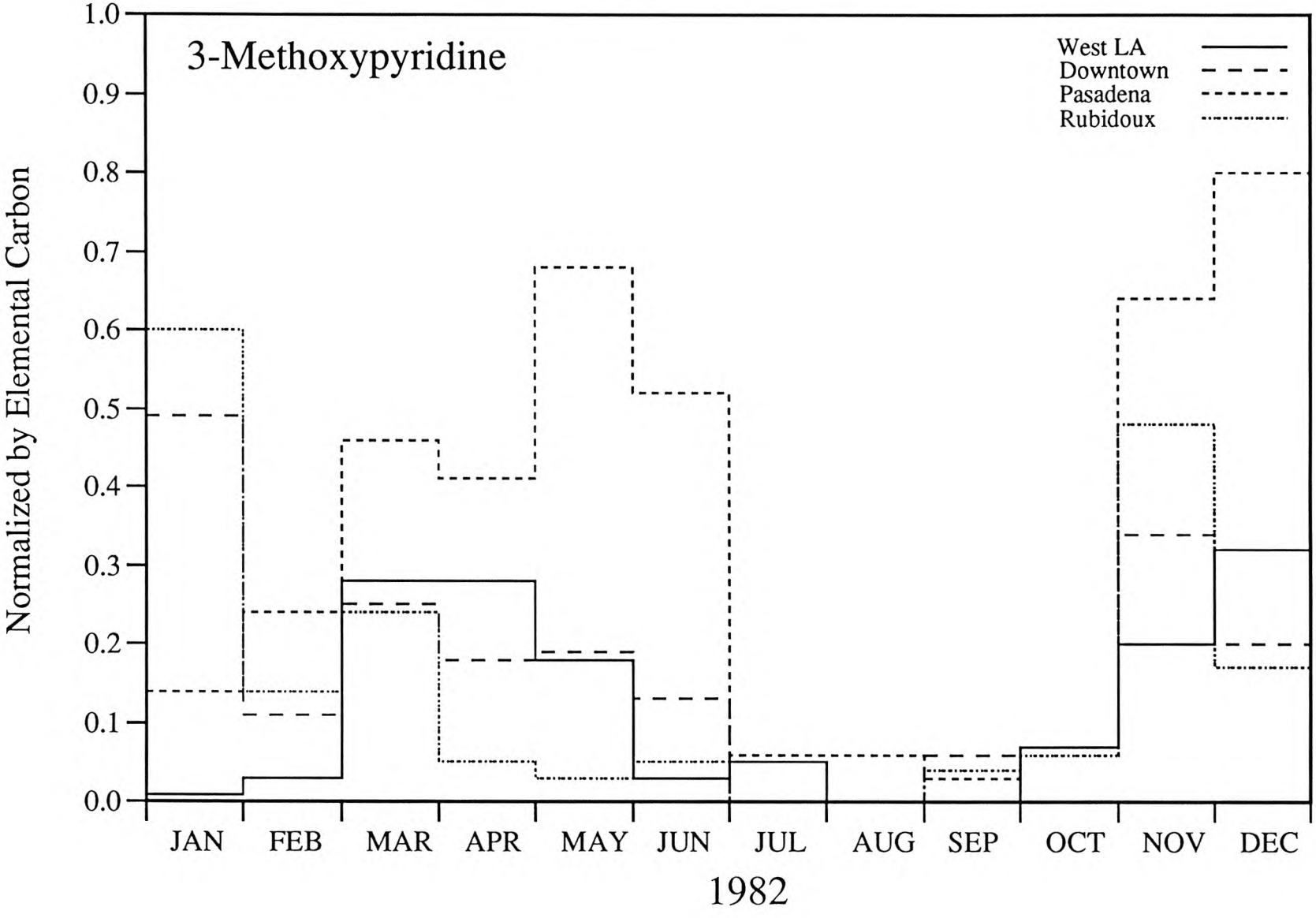

7H-Benz[de]anthracen-7-one
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Benz[a]anthracene-7,12-dione
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982


Benzo[cd]pyrenone
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982

Appendix B10

Normalized Concentration Profiles for N-Containing Compounds


3-Methoxypyridine
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
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MAY
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AUG
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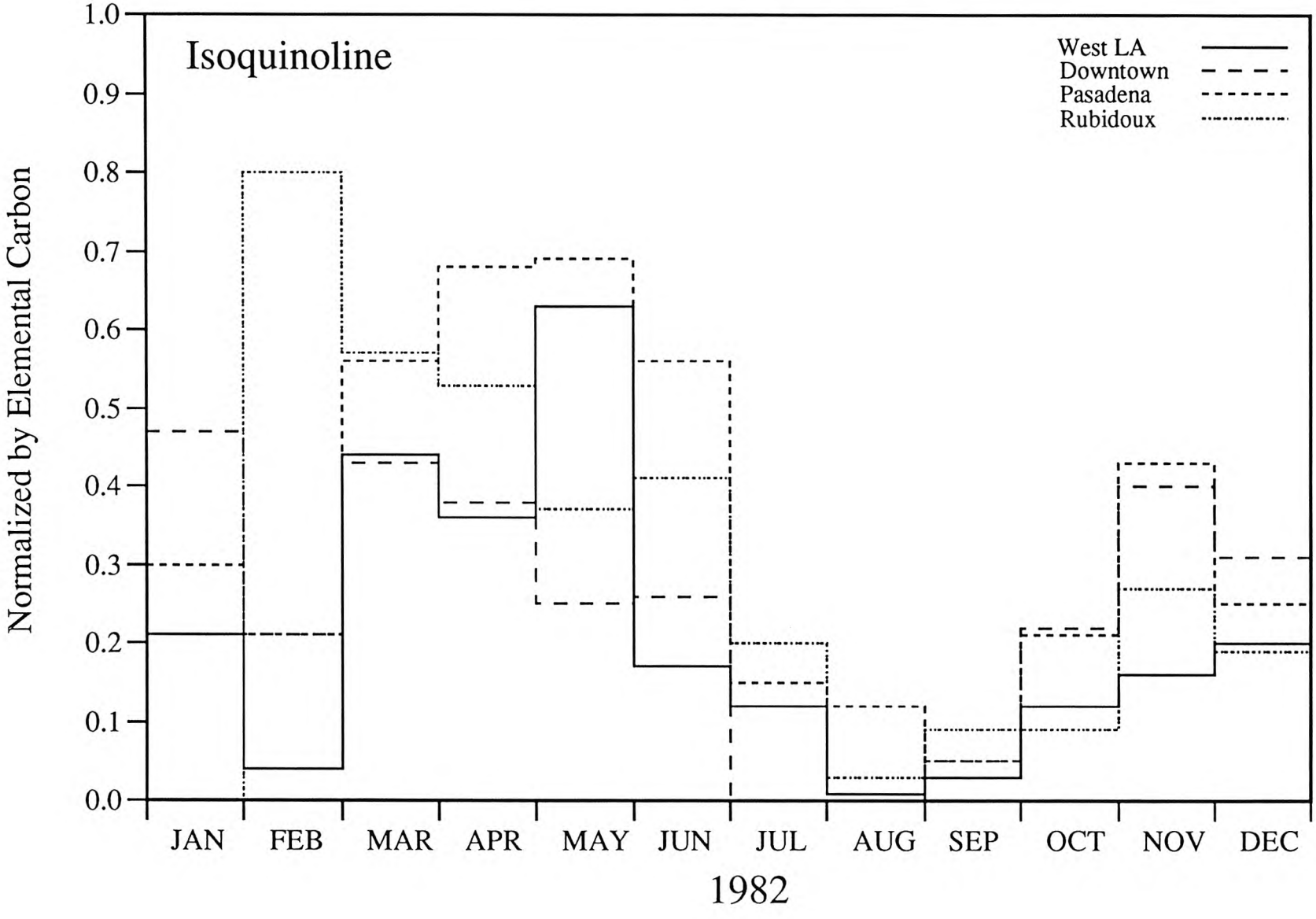
OCT
NOV
DEC
1982


Isoquinoline
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
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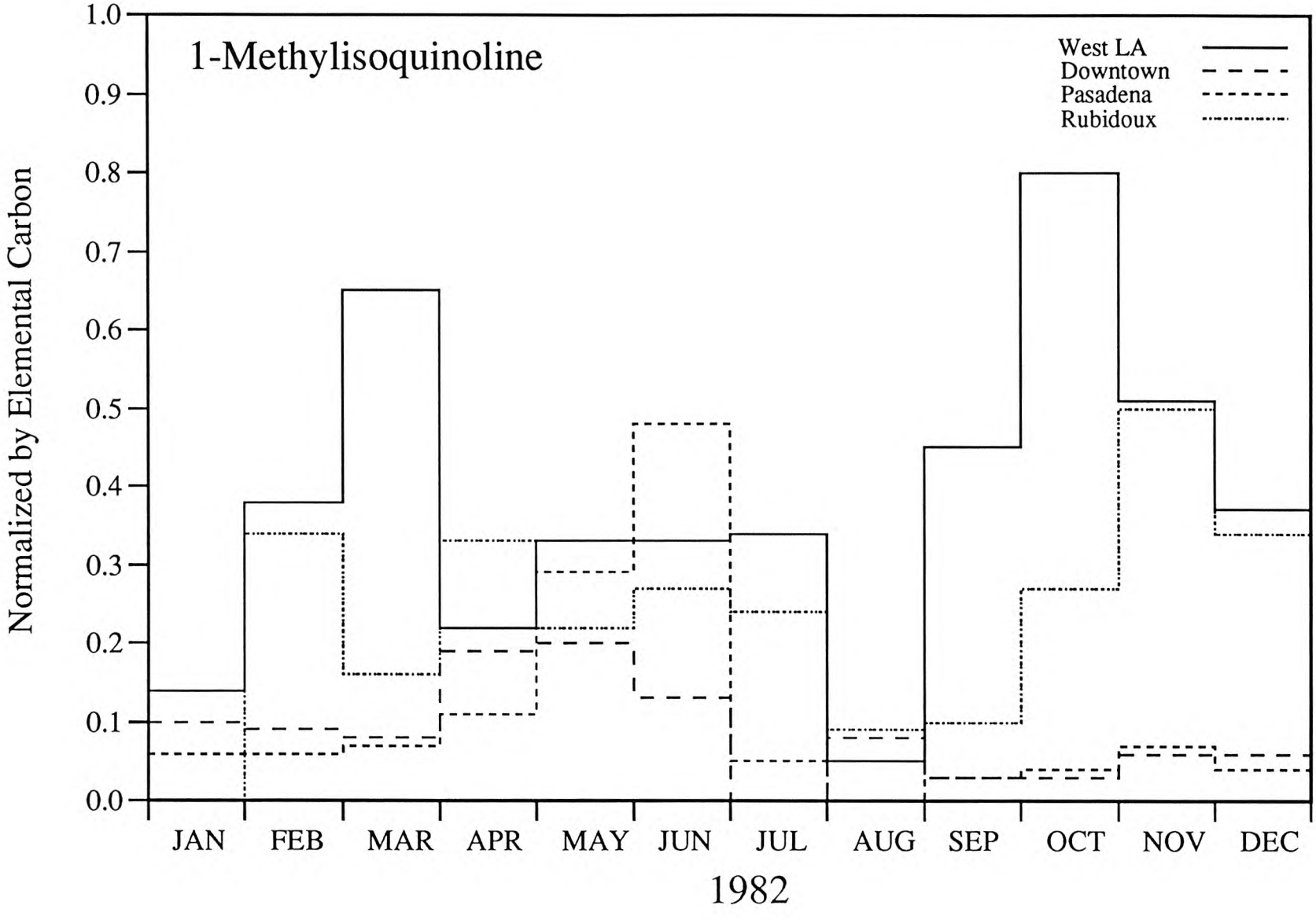
1982


1-Methylisoquinoline
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
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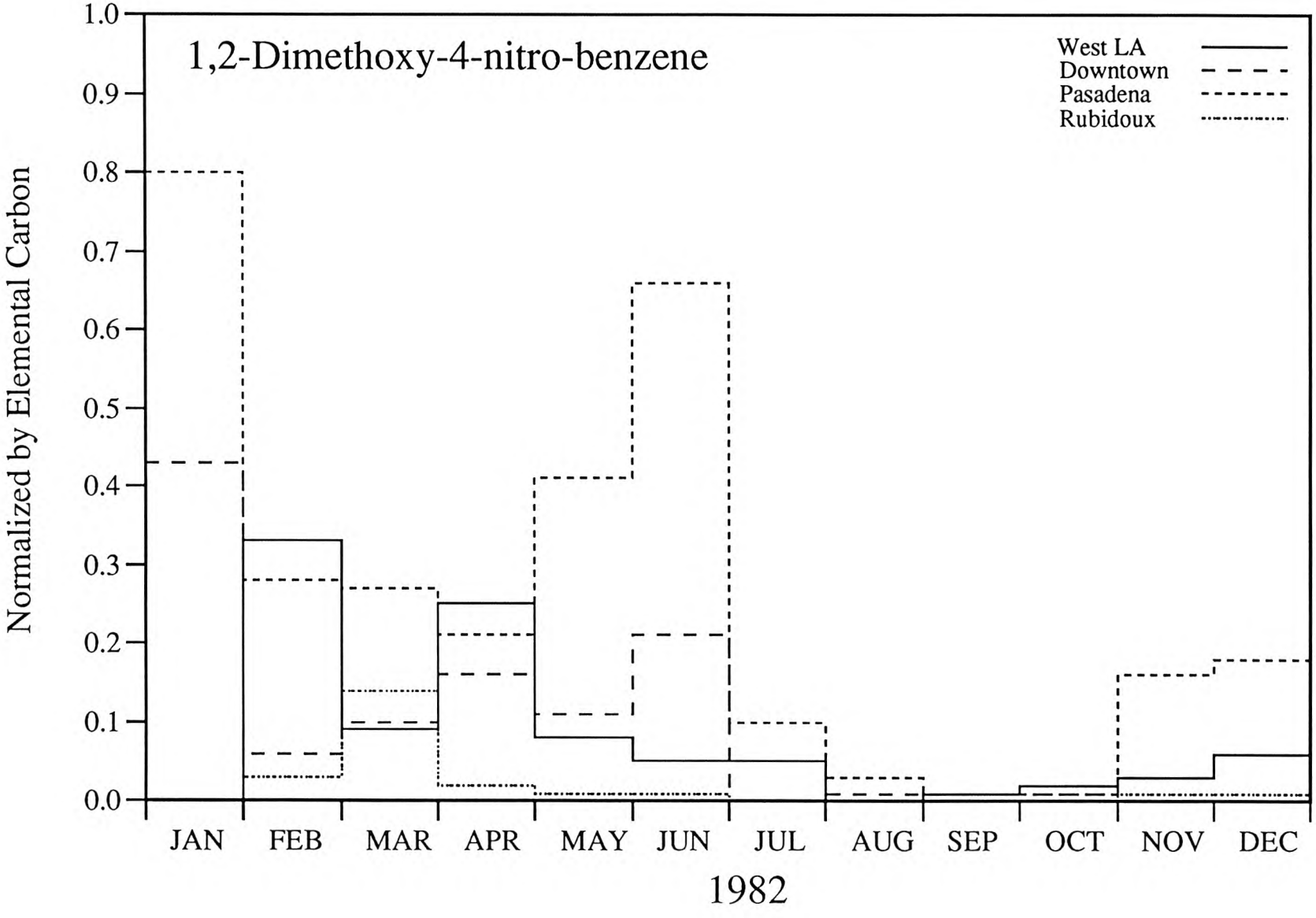
1982


1,2-Dimethoxy-4-nitro-benzene
West LA
Downtown
Pasadena
Rubidoux
Normalized by Elemental Carbon
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1982